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SAMPLING AND ANALYTICAL METHODOLOGY FOR ATMOSPHERIC PARTICULATE NITRATES

Final Report

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ABSTRACT

Environmental conditions that affect atmospheric particulate nitrate sampling were identified, and improved sampling and analytical procedures were developed. Evaluation of potential sources of error in high volume nitrate sampling showed that artifact nitrate formation on commonly used glass filter media was the most serious. Both laboratory and field results demonstrated that high purity quartz filters provide a significant improvement over glass filters and are easily substituted for glass filters in traditional high volume sampling equipment. A sensitive, accurate and rapid nitrate analytical procedure was developed using thermal decomposition of nitrate and chemiluminescent detection of the decomposition products. Ion chromatography was also investigated and found to be sensitive, accurate, reproducible and rapid. Ion chromatography has the added advantage of determining both nitrate and sulfate simultaneously.

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SECTION 1

INTRODUCTION

It has been known for many years that particulate nitrate is a fundamental constituent of our atmosphere and that the nitrate* burden increases considerably as one approaches major urban centers. Questions as to the physiological impact of particulate nitrate were raised at the time of the Chattanooga epidemiological study(1) and have been asked with increasing frequency since that time. However, it has only been in recent months that the correlations between particulate nitrates and certain types of morbidity have become available. Certainly a strong indication that nitrates cause detrimental health effects is the recent finding(2) that airborne nitrates are associated with aggravation of asthma, even in areas where primary ambient air quality standards are not exceeded.

Particulate nitrate has been determined for many years throughout the United States by standard high volume sampling techniques using glass-fiber filters. Robinson and Robbins(3) have estimated the global background nitrate concentration to be on the order of 0.2 $\mu g/m^3$ in the lower atmosphere. Measurements of nonurban nitrate levels by the National Air Surveillance Network(4) generally exhibit a range of annual averages between 0.1 and 1.0 $\mu g/m^3$, with an overall mean of approximately 0.5 $\mu g/m^3$. The lowest nitrate values are found in such areas as Glacier National Park in Montana and Black Hills National Forest in South Dakota, well away from industrial and population centers. Nitrate as nitric acid, has been shown(5) to exist in the stratosphere at concentrations on the order of 0.003 ppm, and is closely associated with the stratospheric ozone layer. There is some evidence(6) that this stratospheric nitric acid can be transported across the tropopause and thus contribute to the background tropospheric nitrate burden.

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*Throughout this report the term "nitrate" will be used interchangeably with "particulate nitrate." Gaseous nitrates will be specified as such.

The level of particulate nitrate in and around major urban centers can be considerably higher than background levels. Based on an 8-year study(7) of the mean concentrations of selected particulate contaminants in the atmosphere of the United States, it appears that nitrate on the average contributes somewhat less than 2 percent of the total suspended particulate weight. The figures vary depending on location. Several representative urban areas were Atlanta at 2.0 $\mu g/m^3$, Chicago at 2.5 $\mu g/m^3$, and Pittsburgh showing 3.0 $\mu g/m^3$.

In certain areas, such as the California southcoast basin, the nitrate levels are even higher, averaging nearly 5 $\mu g/m^3$ in the vicinity of downtown Los Angeles according to NASN results(4). It is interesting to note however, that Gordon and Bryan(8) have reported yearly average nitrate levels in downtown Los Angeles ranging between 9.8 and 15.4 $\mu g/m^3$. Short-term nitrate levels in the eastern basin have been reported as high as 247 $\mu g/m^3$(9).

The major source of atmospheric particulate nitrate is thought to be oxidation of natural and anthropogenic NO and NO_2. The major sinks for particulate nitrate are precipitation scavenging and dry deposition, with the precipitation mechanism estimated(3) to be three times as important as dry deposition on a global basis.

Between the emission of gaseous NO or NO_2 and the ultimate scavenging of the particulate nitrate, there is a highly complex series of reactions which may result in a variety of reaction products prior to the ultimate formation of particulate nitrate. In a recent smog-chamber study of nitrogen oxides reactions conducted by Spicer and Miller,(10) the major initial products of nitrogen oxides reactions in simulated photochemical smog were peroxyacetyl nitrate (PAN) and nitric acid. Excellent nitrogen mass balances were maintained throughout the experiments and the complex mechanisms leading to the formation of organic and inorganic nitrates were investigated. There is little doubt that in the actual atmosphere several other forms of nitrate exist. For example, we have observed(11) low concentrations of alkyl nitrates and peroxypropionyl nitrate in urban atmospheres. We have also detected low levels of particulate organic nitrate in atmospheric aerosol samples(12). Heuss and Glasson(13) have observed another organic nitrate, peroxybenzoyl nitrate (PBzN), in smog simulations. There is also reason to suspect important, albeit low, levels of N_2O_5, a nitrate precursor, in urban atmospheres. It is almost certain that all of these forms of gaseous nitrate ultimately end up as particulate nitrate.

Because of differences likely to be associated with the physiological impact of gaseous and particulate nitrates, it is important to distinguish between the two. The most common means of collecting particulate nitrate is filtration. However, there are a number of known problems involved in filtration sampling of particulate nitrate, and there are also several potentially serious problems which are not so widely recognized. As with any system designed to collect samples by filtration, a most important variable is the filter medium itself. Pate and Tabor(14) have described the characteristics of a wide variety of glass-fiber filters which have been employed by NASN and others for nitrate collection. The manufacture of such glass-fiber filters requires at least six separate steps and usually four participating manufacturers. It is therefore not surprising that substantial variations in the composition and characteristics of these filters often occur. Such variations can affect the accuracy or efficiency of particulate nitrate sampling by

(1) Changing the nitrate filter blank
(2) Affecting the efficiency of particulate collection
(3) Affecting the degree to which particulate nitrate may react with the filter and become unavailable for leaching and analysis
(4) Affecting the extent of extraneous nitrate formation on the filter by nitrate precursors.

Pate and Tabor(14) have reported that the nitrate blank can typically comprise up to 10 percent of the nitrate collection in urban areas, and a considerably higher fraction of nonurban filter samples. However, as long as frequent blank determinations are carried out, this should not be a major difficulty except when sampling extremely low levels of particulate nitrate.

A potentially serious problem in the collection of particulate nitrates was pointed out in 1974(11,15,16). This problem relates to the collection of artifact nitrate on filters due to the interactions of gaseous nitrogen compounds with certain filter materials. Two different studies at Battelle-Columbus have revealed the problem of artifact nitrate collection on certain filter materials. In one study(17) investigating nitrate in auto exhaust, it was found that glass-fiber filters collected almost twice the quantity of nitrate in exhaust as did quartz-fiber filters. Nitrate also appeared on backup filters for both quartz and glass, providing an additional indication of artifact nitrate formation.

In a separate investigation at Battelle, the interaction between nitric acid and a variety of filter materials was studied. The impetus for this study came from the discovery of discrepancies in our atmospheric nitrate data collected on quartz as opposed to glass filters. The results of the study and the implications in terms of atmospheric chemistry and past particulate nitrate data have been reported(11) and presented(15,16) elsewhere. Briefly we find that both the absolute concentrations and also the assumed size distributions of ambient particulate nitrate from many past studies may be in error, due to gaseous nitric acid interference.

One possible explanation for the different collection efficiencies of gaseous nitric acid by quartz and glass filters involves the filter pH. Studies of filter characteristics at Battelle-Columbus(18) have shown that quartz filters are nearly neutral (100 ml filter extracts yields pH of 5-7) while glass filters are often distinctly alkaline (100 ml filter extract yields pH of 9.4). Thus, neutralization and trapping of nitric acid and other acid gases may occur to a greater extent on glass filters than on quartz.

O'Brien, et al.(19) have described a study of photochemical aerosols in the Los Angeles basin in which high-volume samplers and a cascade impactor were employed to determine concentrations and size distributions for NO_3^-, NH_4^+, and $SO_4^=$, among other species. The high-volume sampler and each stage of the cascade impactor employed glass-fiber filters as the collection medium. The results of the study yielded very unusual nitrate size distributions which appeared to be dependent on sampling site. The investigators reported that the strange results could be attributed to formation of artifact nitrate on the glass filters by some gaseous precursor such as nitric acid, and that the true nitrate size distribution was masked in their study by the conversion of gaseous nitrate precursors on the filter.

In addition to interactions between gaseous nitrate precursors and filter media, several other potential interferences with particulate nitrate collection should be considered. For example, certain nitrate precursors may be stable with respect to the filter medium but may be converted by interaction with some component of the aerosol collected on the filter. An example of this type of interaction might be the formation of $NaNO_3$ by the reaction of NO_2 with NaCl collected on the filter. In addition, there may be certain conditions of relative humidity, temperature, atmospheric composition, etc., under which species such as NH_3, NO_2, PAN, N_2O_5, or N_2O could adsorb and/or react with filters or collected aerosol on the filters. Some precursors may be held on the filter by adsorption long enough to be oxidized to artifact nitrate by ozone or some other oxidizing agent.

Another type of interference might involve release of particulate nitrate collected on a filter by conversion to some volatile form. An example might be the reaction of sulfuric acid aerosol with particulate nitrate already collected on the filter to form nitric acid, which could then be lost by volatilization. In the same manner NH_4NO_3, which has a significant vapor pressure, could be lost from particulate collection filters.

Two recent studies which touch on the kinds of interferences just discussed have been reported by Lovelock and Penkett(20) and Chang and Novakov(21). The former investigators found that PAN and PPN do not exist in the clean air over the Atlantic ocean but that clean air has the potential for forming PAN and PPN when exposed to glass surfaces. The potential for PAN formation was greatest on days of high solar intensity, with maximum production during the afternoon hours. An important aspect of this study is the possibility that there are precursors even over the oceans which will form gaseous nitrates given the proper reaction surface. Since the proper reaction surface was glass, the same material used for filters in most high-volume samplers, the possible importance of this reaction mechanisms for particulate nitrate formation must be considered.

Chang and Novakov(21) have studied the formation of particulate nitrogen species due to gas/solid interactions using ESCA. They report the formation of several types of particulate nitrogen due to the reaction of gaseous NO and NH_3 with soot (carbon) particles. Since soot, along with other forms of carbon, is collected on high-volume filter samples, the possibility of forming artifact nitrate from NO and NH_3 reactions exists.

Because of the potentially serious effect of the interferences described above on the accuracy of particulate nitrate data, the U.S. Environmental Protection Agency has initiated a 2-year study at Battelle-Columbus to investigate the impact of these factors on nitrate sampling procedures.

Methods of particulate nitrate analysis were also investigated during the study since most nitrate methods currently in use have important deficiencies. For this reason there is no universally accepted nitrate method and different labs employ many different procedures. What is needed is a fast, reliable, sensitive, specific, accurate and reproducible instrumental method. Our goal was to screen several potential techniques and develop the most promising for ambient nitrate analysis.

The objectives of this program are threefold:

(1) To investigate the effects of environmental variables on the sampling and analysis of particulate atmospheric nitrate
(2) To develop an improved method for the analysis of particulate atmospheric nitrate

(3) To conceive, develop, validate, and optimize a sampling and analysis methodology for atmospheric nitrate.

The experimental aspects of the program have been broken into four phases. A description of each phase is shown below:

Phase I	A laboratory investigation of the factors affecting atmospheric particulate nitrate sampling
Phase II	Development of analytical methodology for atmospheric particulate nitrate
Phase III	Development and evaluation of a sampling procedure for atmospheric particulate nitrate
Phase IV	Optimization, simplification, and delivery to EPA of a validated sampling and analysis methodology.

The remainder of the report will be devoted to a discussion of the experimental results. Each of the above phases of our work will be discussed in turn.

SECTION 2

PHASE I: LABORATORY STUDIES OF ARTIFACT NITRATE COLLECTION ON FILTERS

For purposes of this study we have defined particulate nitrate as any form of nitrate which exists as a filterable particle or adsorbed on a filterable particle under actual atmospheric conditions. This definition excludes all gaseous nitrates and any other nitrogen compounds which might be collected on filters as nitrate due to reaction with the filter material or the collected particulate on the filter.

The goal of the Phase I effort has been to investigate a number of factors which might affect particulate nitrate sampling, and to screen filter materials to determine whether suitable nitrate collection media exist. While novel methods of nitrate collection were not excluded from consideration during the study, we concentrated initially on filtration methods due to the vast apparatus for high volume filter sampling already existing nationwide. If a realistic filtration method for nitrate could be developed, it would be unproductive to study novel techniques which would probably never be employed on a wide scale. Therefore, emphasis has been placed on uncovering factors which affect collection of nitrate on filters.

The major effects and variables that were investigated in the Phase I laboratory study include:

- Gas/filter interactions
- Gas/filtrate interactions
- Gas/soot interactions
- Sampling time
- Sampling rate
- Storage time

Each of these factors is discussed below.

GAS-FILTER INTERACTIONS

The principal goal of this task was to determine the effect of several nitrogen-containing gases on common filter media and to identify types of filters which might be suitable for particulate nitrate sampling in the atmosphere. The experimental procedure involved exposing selected filter materials to ppm concentrations of nitrogen-containing gases in clean air. Nitrogen-containing gases were first diluted with clean cylinder air in a 500-cu-ft Teflon® chamber. The chamber was then evacuated through 47-mm filters of the various materials chosen for study. The pressure and concentration of the nitrogen gas were monitored above and below each filter during the experiment; after exposure the filters were analyzed for NO_3^-, NO_2^-, NH_4^+, and total N. The experimental apparatus is shown in Figures 1 and 2. A schematic of the apparatus is shown in Figure 3. Each filter was typically exposed to more than 1 cubic meter of the dilute nitrogen-containing gas. The concentration of the nitrogen gas was adjusted (low ppm) so that the filter was exposed to approximately the same mass of nitrogen compound as a standard high-volume filter collected in an urban area. The face velocity also was quite similar to a standard Hi Vol.

The nitrogen-containing gases examined include NO, NO_2, HNO_3, PAN, NH_3, and N_2O. The analytical techniques used for these gases are listed in Table 1. N_2O was not determined directly but was prepared by known dilutions of the pure gas. Both dry and humidified conditions have been employed. We have investigated the effect of these nitrogen-containing gases on artifact nitrate formation on a number of filter types. Most of our experiments were conducted with the following filter types:

Glass Fiber - Gelman A
Glass Fiber - Gelman E
Glass Fiber - Gelman AE
Teflon - Millipore Mitex
Polycarbonate - Nuclepore

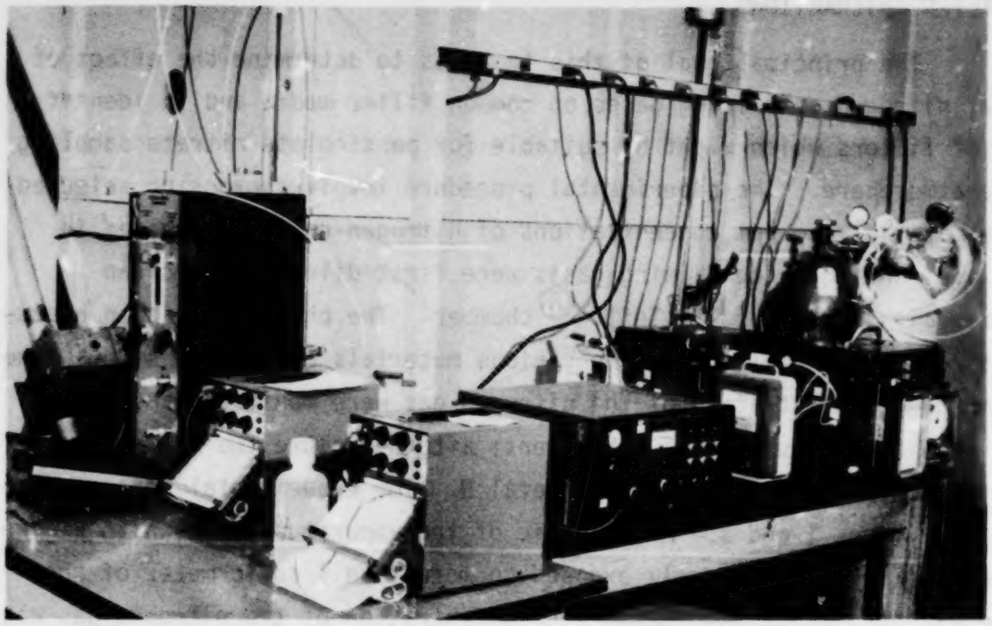


FIGURE 1. PHASE I SAMPLING AND ANALYSIS APPARATUS

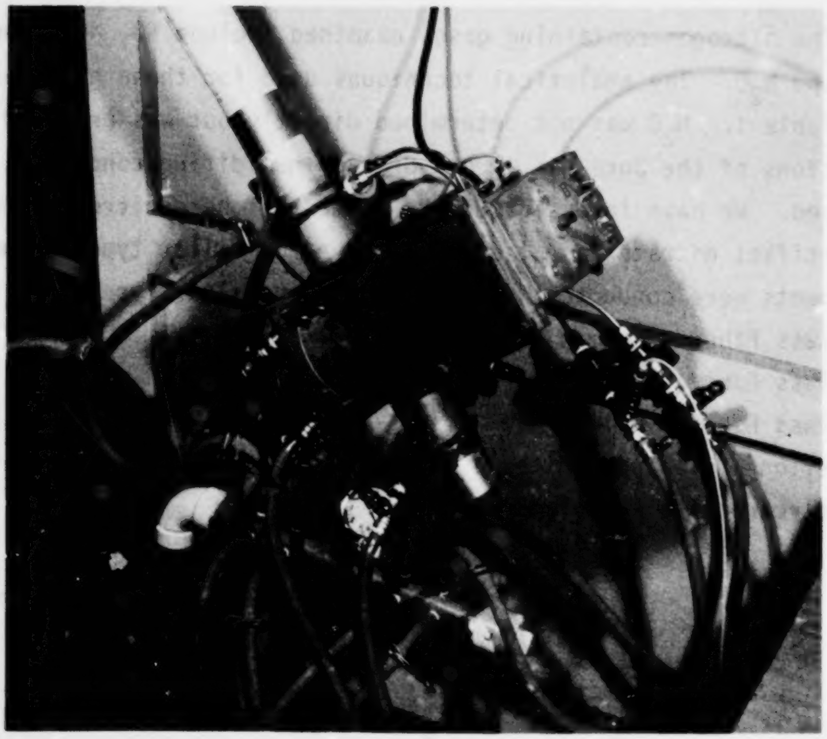
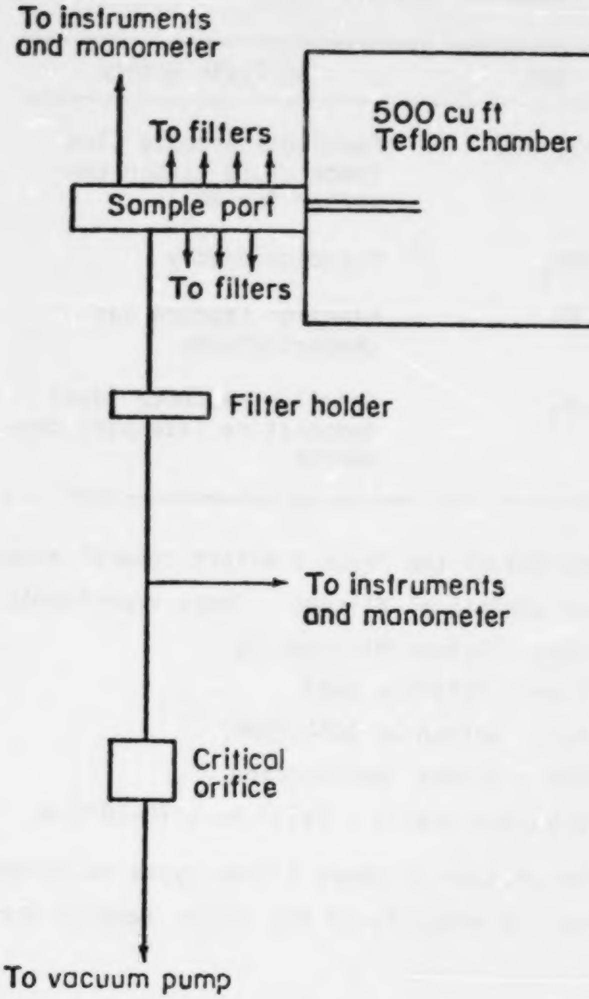


FIGURE 2. CLOSE-UP OF SAMPLING MANIFOLD AND FILTER HOLDERS



To instruments and monometer
To filters
500 cu ft Teflon chamber
Sample port
To filters
Filter holder
To instruments and manometer
Critical orifice
To vacuum pump

Figure 3. Schematic of sampling systems for eight simultaneous filters.

Nylon - Millipore Duralon

Cellulose Acetate - Millipore Celotate

Quartz Fiber - ADL (prototype filter prepared for EPA by Arthur D. Little, Inc.)

TABLE 1. GAS ANALYSIS INSTRUMENTATION

Gas	Analysis Method
NO, NO_2	Chemiluminescence (low temperature carbon converter for NO_2)
HNO_3	Microcoulometry
PAN	Electron Capture Gas Chromatography
NH_3	Chemiluminescence (dual temperature catalytic converter

Toward the end of the Phase I effort, several experiments were conducted with some additional filters. These experiments involved

Quartz Fiber - Gelman Microquartz

Quartz Fiber - Pallflex QAST

Glass Fiber - Gelman AA (EPA Type)

Glass Fiber - Gelman Spectrograde

Cellulose-Backed Quartz - Pallflex E 70-2075 W.

A brief description of each of these filter types is shown in Table 2. The procedures employed for analysis of the filter samples are summarized in Table 3.

TABLE 2. PHYSICAL/CHEMICAL PROPERTIES OF PHASE I FILTER MEDIA

Filter Type	Pore Size(a)	pH(b)	Alkalinity(c)	NO_3^- Blank(d)	Supplier
Cellulose Acetate	1.0	6.65	(1.8×10^{-3})	<0.005	Millipore
Polycarbonate	0.8	6.0	(9×10^{-4})	≤0.006	Nuclepore
Teflon-Mitex	5.0	7.0	0.0	<0.005	Millipore
Glass-AA	NA	8.9	3.24×10^{-2}	<0.005	EPA/Gelman
Glass-A	NA	8.3	4.2×10^{-3}	<0,005	Gelman
Glass-AE	NA	9.4	4×10^{-2}	0.005	Gelman
Glass-E	NA	8.5	3.8×10^{-3}	<0.005	Gelman
Glass-Spectro	NA	7.2	1×10^{-4}	<0.005	Gelman
Nylon	1.0	5.3	(3.6×10^{-3})	≤0.007	Millipore
Quartz-ADL	NA	8.1	1×10^{-4}	<0.005	EPA/ADL
Quartz-QAST	NA	8.1	3.8×10^{-3}	<0.005	Pallflex
Quartz-E 70-2075 W	NA	6.2	(7.6×10^{-3})	<0.005	Pallflex
Quartz-Microquartz	NA	-	-	0.008	Gelman

(a) Pore size in micrometers where applicable.

(b) ASTM-D-202; pH of 100 ml H_2O extract.

(c) Milliequivalents of acid or base required to titrate to neutral point per gram of filter. Parentheses indicate acidic filter.

(d) mg/47 mm filter.

TABLE 3. METHODS OF ANALYSIS

Specie	Method of Analysis
NH_4^+	Gas sensing electrode
NO_2^-	Diazotization-colorimetric
NO_3^-	Brucine sulfate colorimetric/ Ion chromatographic
Total Nitrogen	Modified Kjeldahl digestion

Following the initial experiments all of the filters were analyzed for nitrate and total nitrogen and many were also analyzed for ammonium and nitrite, depending on the gas being studied. However, none of the filters showed any significant increase in the nitrite concentration under any circumstance, and only the nylon filters have shown substantial increases in particulate ammonium levels when exposed to gaseous NH_3. Therefore, nitrite and ammonium analyses were discontinued.

The results of many of our Phase I experiments are shown in Figures 4 and 5. These figures show in bar-graph format the quantity of artifact nitrate found on the filter after exposure to ppm concentrations of the gases shown on the left side of the figure. The experiment number shown at the left of the figure is keyed to a complete tabulation of the experimental conditions contained in the Appendix. In most cases, two or more different concentrations of the nitrogen-containing gas were employed, and frequently both dry and humidified conditions were examined

For purposes of this discussion, we will arbitrarily set the level of significant nitrate interference as ≥ 100 μg. Since we are dealing with a surface effect and a standard 8" x 10" Hi-Vol filter has 40 times the effective collecting area of the 47-mm filters used in this study, a standard Hi-Vol filter might be expected to collect about 40 times as much artifact nitrate as our filters. If our filters collect 100 μg of bogus nitrate, a standard Hi-Vol might collect 4000 μg of artifact. Assuming a 24-hour sample volume of 2000 m^3 for a standard Hi-Vol filter, the level of nitrate interference would be 2 μg/m^3. This concentration approaches the average NO_3^- concentration measured in many urban areas and thus constitutes a major interference.

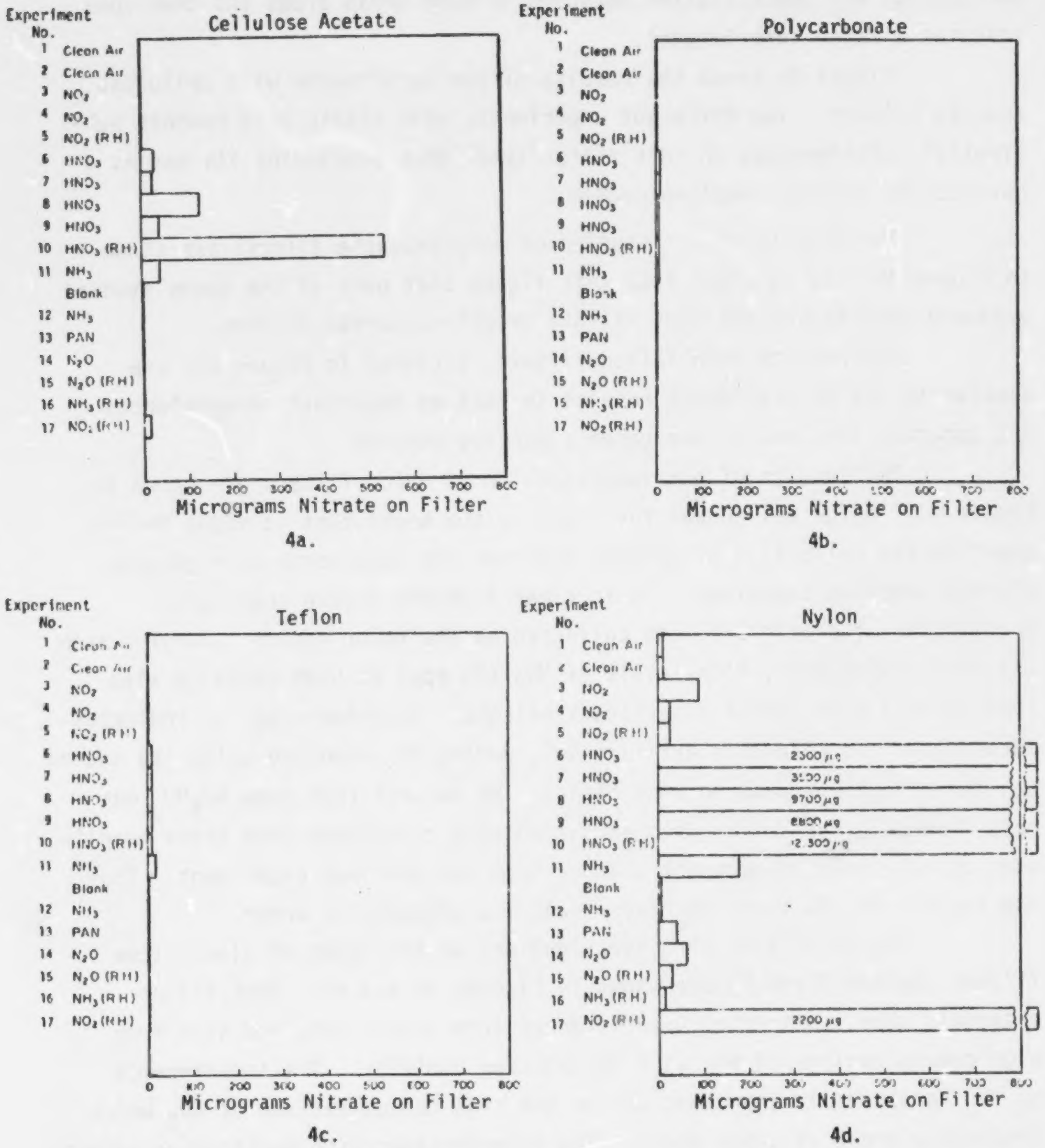
Figure 4a shows the results of our experiments with cellulose acetate filters. Two different experiments with nitric acid exhibit substantial interferences on this filter type, thus precluding its use as a particulate nitrate sampling medium.

The results of our studies of polycarbonate filters are shown in Figure 4b. It is clear from this figure that none of the gases studied produced significant artifact nitrate on polycarbonate filters.

The results with Teflon filters, pictured in Figure 4c, are similar to the polycarbonate results in that no important interferences are apparent from any of the gaseous species studied.

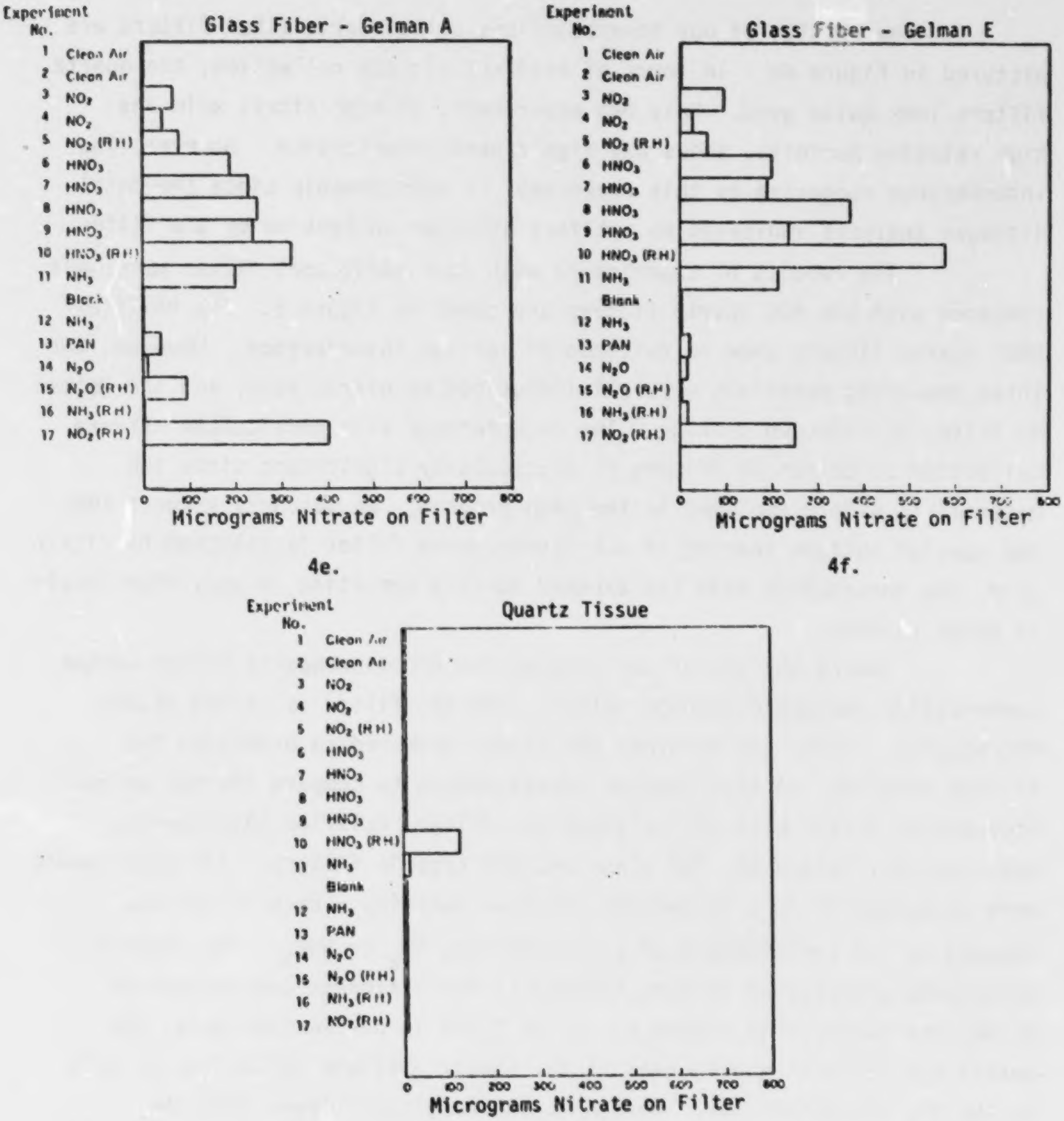
The results of our investigation of nylon filters are shown in Figure 4d. Nylon was chosen for study in the hopes that it might provide quantitative collection of gaseous nitrates and thus serve as a gaseous nitrate sampling technique. It is clear from the figure that large quantitites of nitric acid are collected by the nylon medium. Judging from the final experiment, high levels of NO_2 (30 ppm) at high humidity also lead to very high levels of artifact nitrate. Experiment No. 11 indicates formation of considerable artifact $NO^-{}_3$ during NH_3 exposure while the second and third NH_3 runs show no such effect. We suspect that some NH_4NO_3 may have formed in our Telfon chamber during this experiment from trace quantities of HNO_3 remaining in the chamber from the previous experiment. Thus the results of the first NH_3 experiment are probably in error.

The results of our investigations of two types of glass-fiber filters (Gelman A and E) are shown in Figures 4e and 4f. Both filter materials show substantial interferences from nitric acid and also from high concentrations of NO_2 at high relative humidity. The interference by NO_2 is extremely important due to the high concentrations of NO_2 which frequently occur in urban areas. The interferences with particulate nitrate collection on these alkaline-surfaced glass filters makes them rather poor choices for nitrate sampling in the atmosphere.



4a. 4b. 4c. 4d.

Figure 4. Gas-filter interactions.



4e.

4f.

4g.

Figure 4. Gas-filter interactions

The results of our investigations using quartz-fiber filters are pictured in Figure 4g. In terms of artifact nitrate collection, the quartz filters look quite good. Only one experiment, at high nitric acid and high relative humidity, shows any significant interference. However, the interference suggested by this experiment is questionable since the total nitrogen analysis indicated no artifact nitrogen collection by the filter.

The results of experiments with four additional filter materials compared with the ADL quartz filters are shown in Figure 5. The Pallflex QAST quartz filters show no evidence of serious interference. However, the three remaining materials were all influenced by nitric acid, and the Gelman AA filter by nitrogen dioxide. The interference with particulate nitrate collection on Gelman AA filters is particularly significant since the material is widely employed in the NASN program. We strongly suspect that the special surface coating of the Spectrograde filter is attacked by nitric acid, the interaction with the exposed surface resulting in very high levels of bogus nitrate.

Toward the end of our program the ADL microquartz filter became commercially available through Gelman. The new filter is called Gelman Microquartz. Since the original ADL filter appeared so promising for nitrate sampling, we initiated an investigation to compare the new Gelman Microquartz filter with the original ADL filter, Pallflex QAST quartz, Spectrograde, Gelman AE, MSA glass and EPA type AA filters. All experiments were conducted at 30 ± 10 percent relative humidity, Each filter was exposed to 1-2 cubic meters of air containing NO_2 or HNO_3. The results of nitrate analyses of filters exposed to two different concentrations of NO_2 are pictured in Figure 6. As we found in our earlier work, ADL quartz and Pallflex quartz exhibit the lowest artifact collection at both of the NO_2 concentrations. Gelman AE and AA glass filters show the greatest artifact collection in these NO_2 experiments. In both experiments, the Gelman variation of the Microquartz filter collected more artifact nitrate than either the original ADL Microquartz or the Pallflex quartz filters. The only filter which approached our interference criterion of 100 μg was Gelman AE in the high concentration NO_2 experiment.

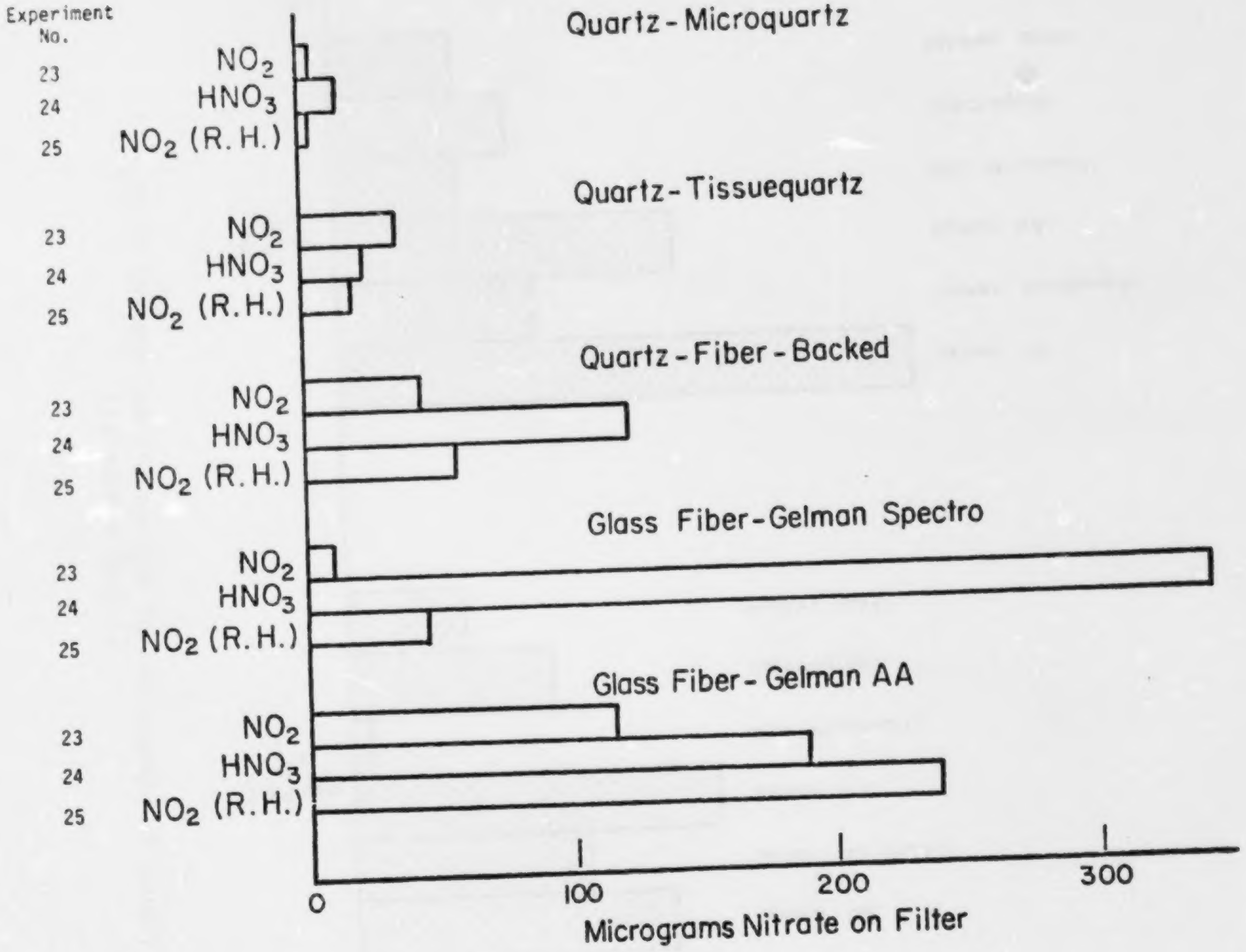


Figure 5. Gas-filter interactions

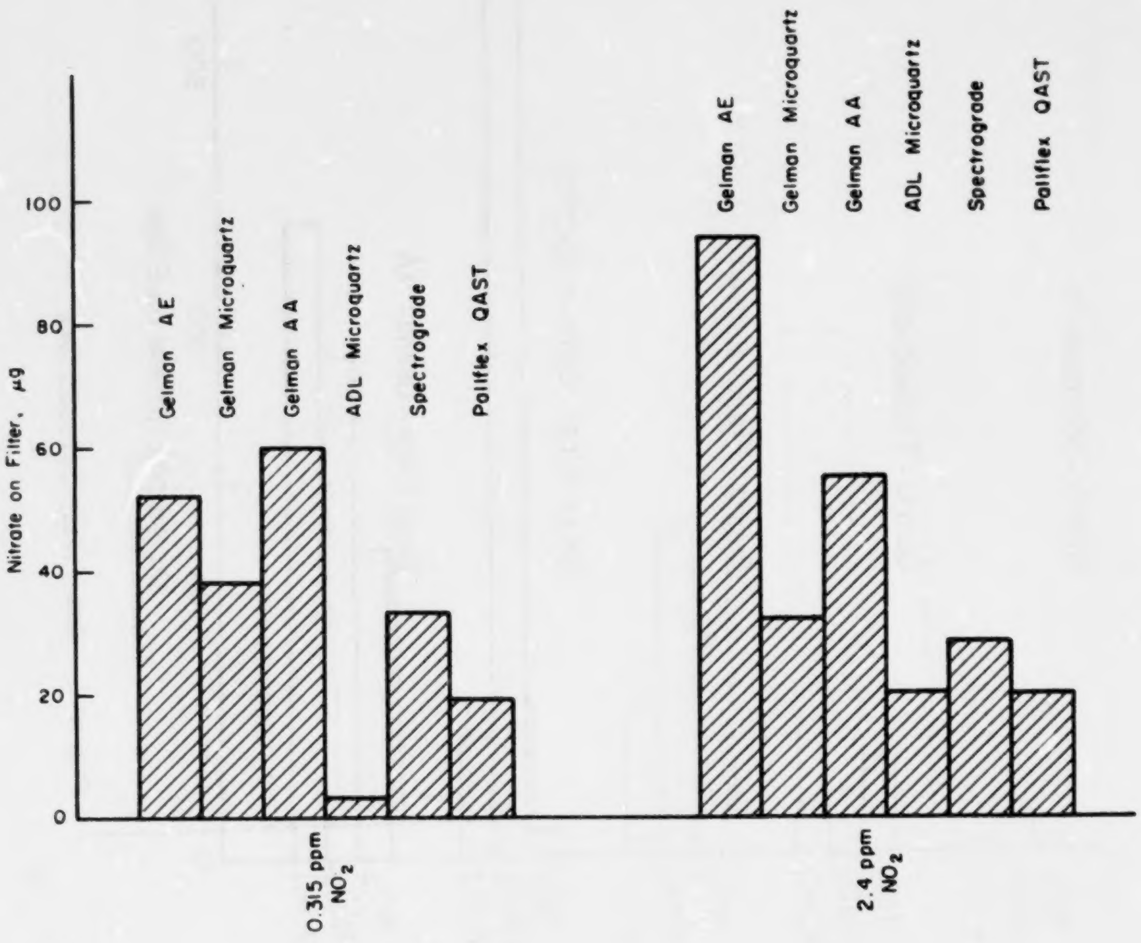


Figure 6. Comparison of various filters exposed to NO_2. (1-2 m^3 exposures)

The results of nitric acid exposures at 0.27 ppm and 3 ppm are shown in Figure 7. In these experiments, all three of the glass-fiber filters exceeded the interference criterion, and the Gelman microquartz exceeded it in one case and equalled it in the other. It seems likely that the commercial Microquartz is inferior to the original prototype filter for nitrate sampling. Only ADL quartz and Pallflex quartz filters showed minimal interference in these experiments. In agreement with our previous results (e.g., Figure 5 and Table 4), less artifact is collected on ADL than on Pallflex. The results of these additional NO_2 and HNO_3 experiments confirm our earlier studies that ADL Microquartz and Pallflex QAST quartz are clearly superior to glass fiber filters for nitrate sampling.

Breakthrough Experiments

The interaction of the gaseous nitrates PAN and nitric acid with filter materials is of particular concern in this study because: (1) We have observed these gases at relatively high concentrations (50 ppb) in urban atmospheres and (2) They could easily form artifact nitrate by simple adsorption on filters. In addition to the experiments already reported with these two gases, we have carried out several experiments using a different technique. In these experiments either PAN or nitric acid was generated at low (sub-ppm) concentrations in a 200 liter glass smog chamber. The mixture was then pulled through the filters under study. The concentration of PAN or nitric acid in the chamber was determined at the start of the experiment, and then the concentration was monitored down stream of the filters. After an initial induction period during which the gaseous nitrates were removed by the filter, breakthrough occurred and the concentration downstream of the filter slowly increased to the level in the chamber. The breakthrough response curve was integrated and used to calculate the mass of gaseous nitrate removed by the filter. A system blank (same apparatus but filter holders empty) was run for each gas and subtracted from the filter results.

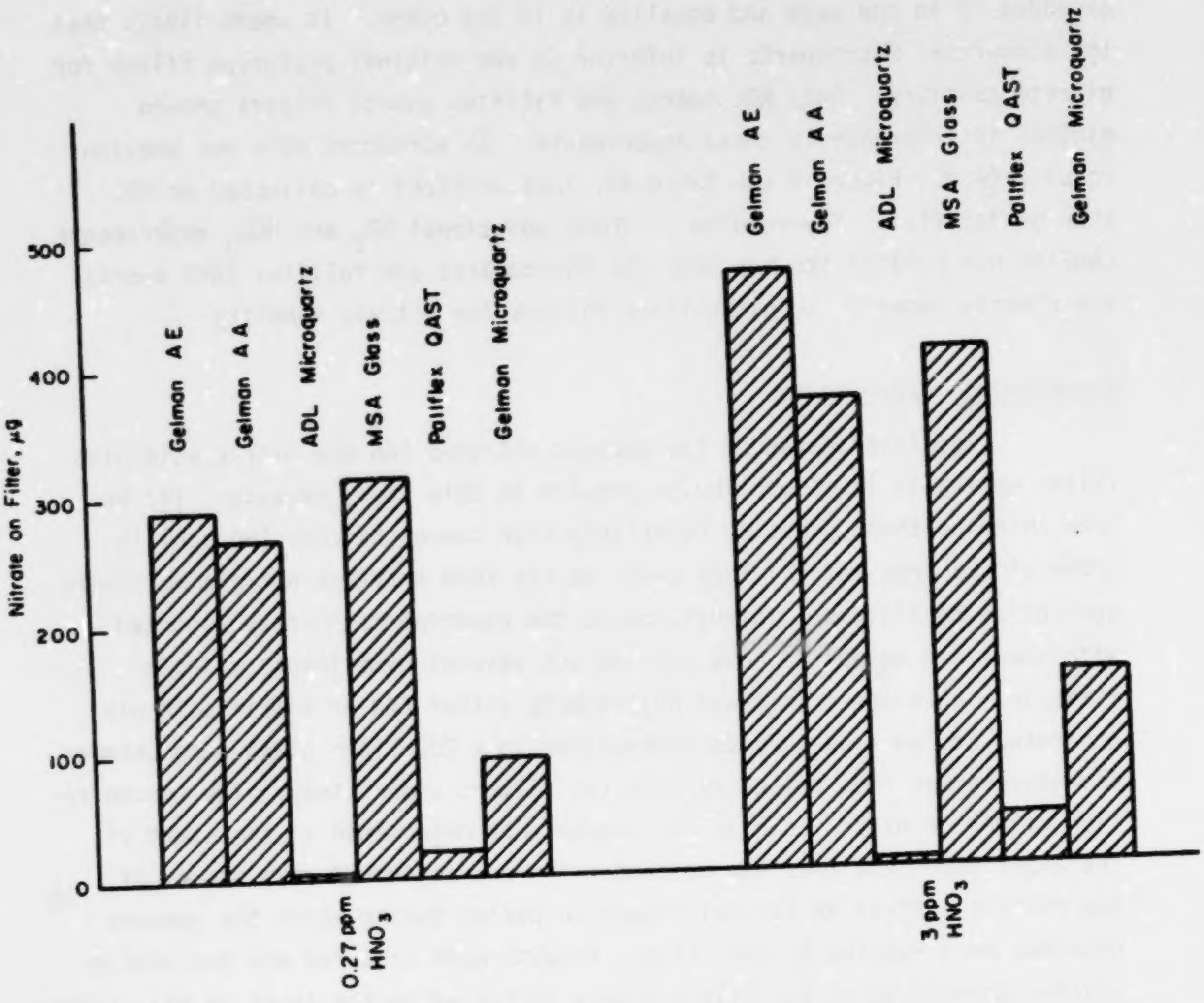


Figure 7. Comparison of various filters exposed to HNO_3.
(1-2 m^3 exposures)

The results of the filter adsorption experiments for nitric acid are shown in Table 4. These data are in qualtitative agreement with the nitric acid results presented earlier, i.e., nitrate interference due to nitric acid adsorption on Teflon, quartz and polycarbonate filters is negligible. Interference due to adsorption on the two types of glass filters can be serious.

TABLE 4. FILTER ADSORPTION RESULTS FOR NITRIC ACID

Filter Material	Nitrate Removed by 47-mm Diameter Filter, μg
Teflon	0.13
Quartz	0.11
Polycarbonate	2.8
Glass (Gelman E and AE)	Very large (no breakthrough after 8 hours of sampling)

PAN was generated at ambient concentrations for the breakthrough experiments by the photolysis of ethyl nitrite in dry air. A gas chromatograph equipped with an electron capture detector was used to monitor the PAN. The mass of PAN removed by the various filters is shown in Table 5, along with a list of the potential artifact nitrate which might be expected under actual ambient sampling conditions for each filter type. These data indicate, as did the results from experiment 13, that nitrate interference due to PAN adsorption is unimportant for the filters studied.

Nitrogen Balance

A check of the filter nitrogen balance for nylon, Gelman A and Gelman E filters was carried out using the results of experiment numbers 6, 7, 8, 9, 10 and 17. These experiments were chosen because the quantity of artifact nitate found on the filters was well above the filter blank.

TABLE 5. PAN-FILTER INTERACTION STUDY RESULTS

Filter Material	PAN Adsorbed, µg	Potential Hi-Vol. Nitrate Interference, µg
Quartz - ADL	0.003	.065
Quartz - Pallflex QAST	0.006	.13
Quartz - Pallflex E 70-2075 W	0.009	.20
Glass - Gelman AA	0.35	7.6
Glass - Gelman A	0.010	.22
Glass - Gelman E	0.012	.26
Glass - Gelman AE	0.18	3.9
Glass - Gelman Spectrograde	0.020	.43
Nylon - Duralon	0.008	.17
Cellulose Acetate	0.007	1.3
Polycarbonate	0.007	.15
Teflon	0.005	.11

The percentage of the total filter nitrogen which could be accounted for as nitrate-nitrogen has been calculated for these three filter types, taking both the nitrate and total nitrogen blank into account. The average accountability for the six experiments was

Nylon - 71 percent
Gelman A - 127 percent
Gelman E - 93 percent.

The value shown for nylon is probably not very accurate due to the large total nitrogen blank correction. The high Gelman A percentage seems to result from low total nitrogen analyses of Gelman A filters for two of the experiments. The reason for the low analytical results is unknown.

Effect of Filter Saturation

All of the experiments described above have involved sampling about 1 cubic meter of air containing ppm quantities of some nitrogeneous gas through individual filters. While the results of these experiments will be used to indicate types of filters suitable for particulate nitrate sampling, still it would be useful to understand the relationships among artifact nitrate formation, sample concentration and sample volume. The results of a preliminary investigation of these relationships are listed in Table 6. The experiment (No. 22) shown in this table was designed to investigate the effect on filters of sampling low nitric acid concentrations over longer exposure times. Approximately 4 m^3 of the sample mixture (350 ppb nitric acid in air) passed through the filters. Based on the 100 μg

TABLE 6. RESULTS OF LOW CONCENTRATION NITRIC ACID EXPERIMENT (350 ppb HNO_3)

Filter Material	NO_3^-, mg	NH_4^+, mg	Total N, mg
Glass (Glaman AE)	0.23	<0.003	0.04
Quartz (ADL Microquartz)	<0.005	<0.003	0.01
Quartz (Pallflex QAST)	0.086	<0.003	0.03

interference criterion put forward earlier, the glass filter shows significant artifact nitrate. The ADL microquartz was unaffected by the dilute gaseous nitric acid, while the Pallflex tissuequartz collected artifact nitrate at levels approaching the 100 μg interference criterion. These data can be compared with the results of a second nitric acid experiment at a similar concentration. A side-by-side comparison of these two experiments is presented in Table 7.

TABLE 7. COMPARISON OF LOW CONCENTRATION NITRIC ACID EXPERIMENTS WITH DIFFERENT SAMPLE VOLUMES

Filter Material	0.315 ppm HNO_3[(a)]	0.27 ppm HNO_3[(b)]
	NO_3^-, mg	NO_3^-, mg
Gelman AE	0.23	0.29
ADL Microquartz	<0.005	<0.005
Pallflex QAST	0.086	0.020

(a) $4m^3$

(b) $1.3m^3$

The results of the two experiments are remarkably similar, considering that they were conducted over a year apart. It is clear that the ADL Microquartz was not affected by exposure, while the AE glass filter was seriously influenced. The effect on Pallflex was variable, but in neither case was the interference criterion exceeded. The amount of NO_3^- found on the Pallflex filter increased by a factor of four when the mass of HNO_3 passed through the filter was quadrupled. However, the Gelman AE filter appeared to saturate at the lower concentration and showed no gain in NO_3^- with quardrupling of the HNO_3 through-put. The saturation of the filter surface with artifact nitrate is important to our understanding of artifact collection and will be explored further.

Saturation of the surface active (basic) sites of filters by artifact nitrate was suggested in our discussion of Table 6 and 7. If saturation does occur, then the influence of artifact collection on ambient nitrate measurements will go through a maximum, which will occur at the time of saturation. Additional sampling through the saturated filter will reduce the impact of artifact nitrate on the ultimate calculated nitrate concentration. Therefore, short term collections during periods of high precursor concentrations may result in the most serious sampling errors.

In our laboratory studies, filter saturation could make the artifact collection efficiency appear artifically low, thereby masking the true extent of the interference. We have investigated this phenomenon with NO_2 and HNO_3 using a glass and a quartz filter. The results of our studies with NO_2 are shown in Figure 8. In these experiments, sub-ppm concentrations of NO_2 (RH = 20%) were sampled through quartz and glass filters for different times. The quantity of artifact nitrate collected on each filter is plotted versus the mass of NO_2 which passed through the filter. As we might have expected from our earlier results, the quartz filter saturates earlier and at lower levels than the glass filter. From previous results we would expect the ADL quartz and Pallflex quartz to saturate even more rapidly than the Gelman Microquartz. Based on Figure 8, the Gelman Microquartz appears to reach saturation at about 110 μg/47 mm filter. The AA glass is not yet saturated even at 210 μg.

The results of a similar set of experiments with nitric acid are depicted in Figure 9. In these experiments, the filters were saturated even at the lowest nitric acid exposure, so that the left-hand portion of the curves were extrapolated to zero. The filters were certainly saturated by exposure to 2 mg HNO_3, but the amount required for saturation may have been much less than this. Other data (from Figure 7) suggest that both the AA and Gelman Microquartz filters become saturated with exposure to less than 1 mg HNO_3. Since AA glass seems to saturate at about 320 μg artifact NO_3^-, the filter is at least 30 percent efficient at scrubbing gaseous nitric acid, up to the saturation point. Results of the breakthrough experiments described earlier demonstrate that the glass filters are actually 100 percent efficient at collecting nitric acid up to the saturation point.

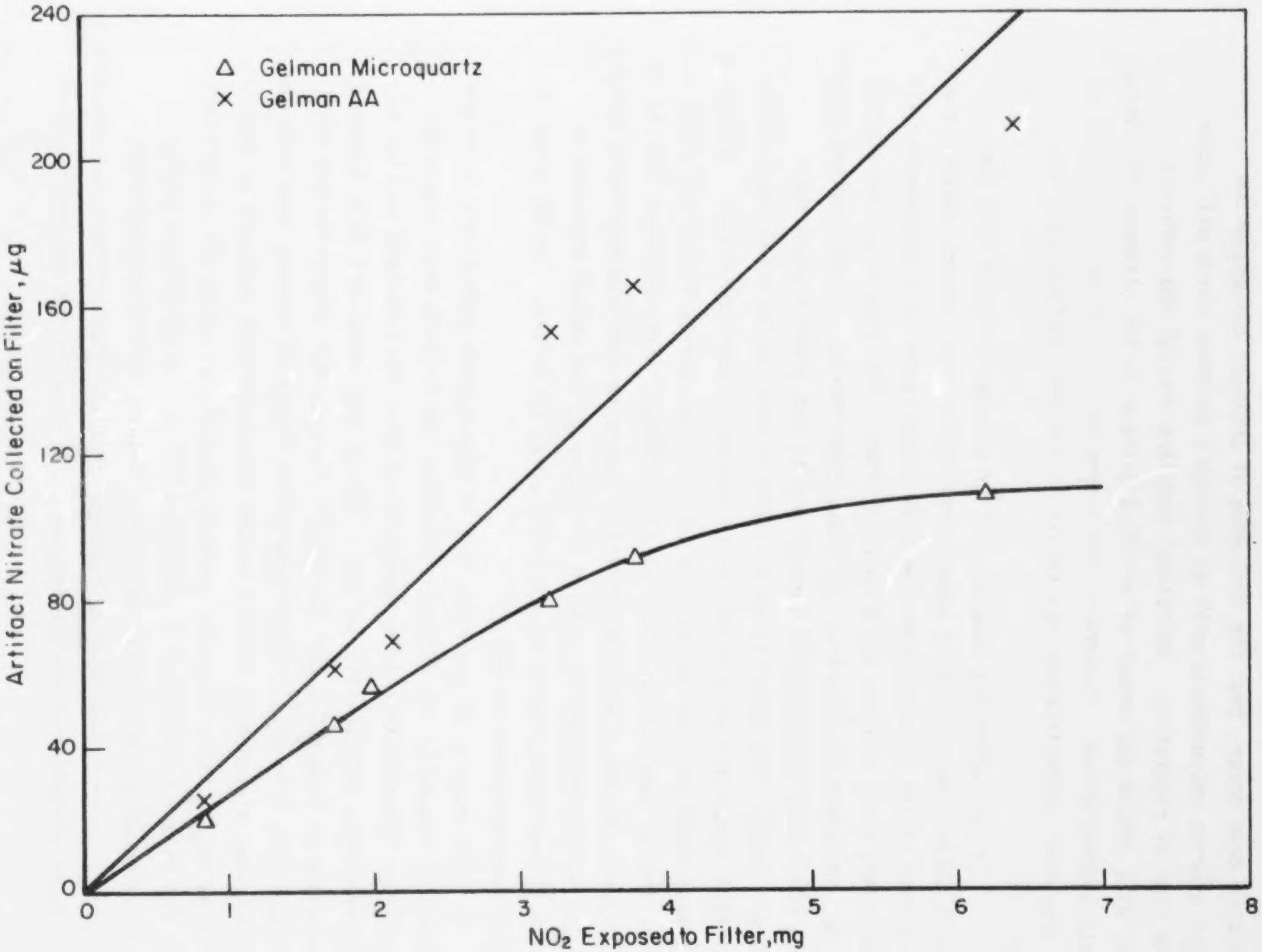


Figure 8. Artifact nitrate as a function of NO_2 exposure.

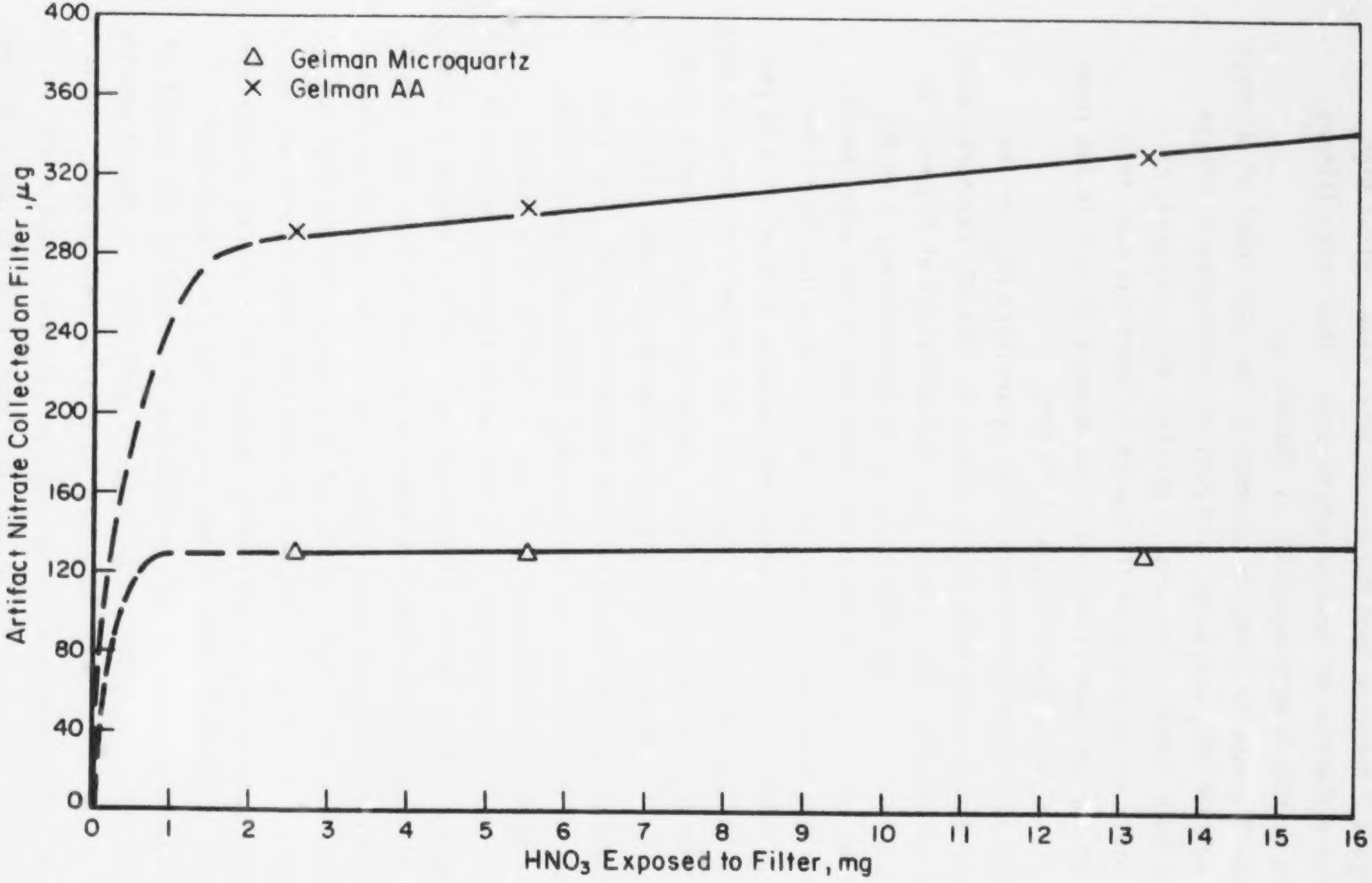


Figure 9. Artifact nitrate as a function of HNO_3 exposure.

The data in Figure 7 indicate that MSA and AE glass have similar high efficiencies for collection of gaseous nitric acid. Thus these filters should saturate at nitric acid exposures of 300-400 μg.

Gelman Microquartz seems to saturate at the same level of artifact NO_3^- for both NO_2 and HNO_3 exposures, although the efficiency of nitric acid removal is much higher. The mass of artifact NO_3^- collected at saturation probably varies somewhat from batch to batch and even from filter to filter for the same filter type, but appears to fall in the range of 100-150 μg for 47 mm Gelman Microquartz filters.

Gelman AA filters saturated at ∿320 μg artifact NO_3^- in the nitric acid experiments shown here and in Figure 7. The NO_2 exposures were not sufficient to saturate this filter, but extrapolation of Figure 8 to ∿320 μg artifact NO_3^- indicates that exposure to approximately 8 mg NO_2 would be required for saturation under the conditions of our experiments. The results of these experiments indicate that a 47 mm Gelamn AA filter will saturate at ∿320 μg artifact nitrate when exposed to 80 m^3 of 0.05 ppm NO_2 in air or 0.002 ppm HNO_3 in air. Obviously the filter will saturate more rapidly when both NO_2 and HNO_3 are present. Based on Figures 8 and 9, even smaller volumes will suffice to saturate the Gelman Microquartz filter.

Extrapolating these results to the surface area and flow rates of typical high volume samplers, it seems highly likely that both filter types would approach saturation over a 24 hour collection in a typical urban area. Saturation of a Gelman AA Hi Vol would typically result in ∿5 $\mu g/m^3$ artifact nitrate. Gelman Microquartz could collect nearly 2 $\mu g/m^3$ of artifact. Although these values are based on extrapolations, the assumptions behind the extrapolations seem logical. Further discussion of these data will be reserved for a later section of this report dealing with our field measurements. The Phase I study of gas/filtrate interactions was not designed to quantitate nitrate interference so much as to screen prospective filter materials in terms of their suitability for particulate nitrate sampling. A subsequent phase of this program has investigated the impact of artifact nitrate formation under actual ambient conditions and should provide a much more accurate estimate of the extent of nitrate interference. Indicaitons from our laboratory data suggest that we saturated the surface sites of many of the filters early in our experiments by using ppm quantities of precursor gases. Under such conditions the apparent artifact collection efficiency is lower than expected under ambient sampling conditions. In other words, we believe that the percentage of artifact nitrate interference reported here may only be the lower limit to that expected under ambient sampling conditions.

GAS-FILTRATE INTERACTIONS

As mentioned in the introductory section of this report there are several possible interactions between gases or aerosols in ambient air and the particulate matter (filtrate) collected on high volume filters, which could result in either positive or negative interference with particulate nitrate determinations. The interaction between gases or aerosols passing through a filter and the collected filtrate was investigated by exposing actual ambient filter collections to exaggerated concentrations of several potential interferences. The concentration of nitrate on the filters was determined both before and after exposure, so that a simple comparison should reveal any significant interferences. In terms of experimental procedure, ambient Columbus aerosol was collected by Hi Vol. sampling on several 142-mm filters. 47-mm circles were cut from these filters and exposed to candidate gases in the same apparatus used for the gas-filter interaction studies. The results of nitrate analyses of these filters are shown in Table 8. The lack of consistent changes in NO_3^- levels upon exposure indicates that interactions between candidate substances (NH_3, H_2SO_4, HNO_3, NO_2) and the collected particulate are not significant. The one exception seems to be cellulose acetate in experiment 20. Both NO_3^- and total N increased significantly during this experiment.

GAS-SOOT INTERACTIONS

The potential role of soot collected on Hi Vol filters in converting gases such as NO_2 and NH_3 to nitrate has been discussed by Chang and Novakov(21). The importance of gas-soot interactions was investigated in this study by loading 142-mm Gelman A filters with 4 mg of finely dispersed carbon-black and then passing approximately 2 m^3 of air containing ppm levels of NH_3 or NO_2 through several 47-mm diameter circles cut from these filters.

TABLE 8. PRESOILED FILTER ANALYSES (mg/FILTER)

Filter Material	NO_3^-	NH_4^+	Total N
Presoiled Filters (Before Exposure)			
Glass-Gelman AE (1)(a)	0.36	0.007	0.10
Glass-Gelman AE (2)	0.26	0.006	0.10
Cellulose Acetate (3)	0.037	0.014	0.06
Cellulose Acetate (4)	0.047	0.027	0.09
Quartz-Microquartz (5)	0.038	0.028	0.06
Quartz-Tissuequartz (8)	0.12	0.072	0.15
Exposed Filters			
Experiment No. 18 - 11.5 ppm NH_3			
Glass-Gelman AE (1)	0.35	0.005	0.13
Cellulose Acetate (3)	0.033	0.016	0.10
Quartz-Microquartz (5)	0.025	0.026	0.07
Experiment No. 19 - 97 $\mu g/m^3$ H_2SO_4			
Glass-Gelman AE (1)	0.28	0.068	0.17
Cellulose Acetate (3)	0.030	0.045	0.14
Quartz-Microquartz (5)	0.055	0.10	0.14
Quartz-Tissuequartz (8)	0.12	0.19	0.20
Quartz-Microquartz (unsoiled)(b)	<0.005	0.092	0.11
Experiment No. 20 - 3.4 ppm HNO_3			
Glass-Gelman AE (1)	0.40	0.011	0.13
Cellulose Acetate (3)	0.26	0.028	0.22
Quartz-Microquartz (5)	0.037	0.025	0.06
Experiment No. 21 - 19.5 ppm NO_2			
Glass-Gelman AE (1)	0.22	0.013	0.10
Cellulose Acetate (4)	0.043	0.021	0.07
Quartz-Microquartz (5)	0.028	0.020	0.05
Quartz-Tissuequartz (8)	0.11	0.072	0.14

(a) Numbers in parentheses identify ports used during presoiling.

(b) SO_4^{-2} was 0.087 for this filter.

Analysis of these filters gave the results shown in Table 9. The nitrate level increased after exposure to NO_2, however, the magnitude of the increase is below the level of artifact nitrate formed during exposure of clean Gelman A filters alone. Thus the gas-soot interaction does not appear to contribute significant quantities of artifact nitrate under our study conditions. Other types of soot were not examined, however so that we cannot totally dismiss the possibility of an interaction under some conditions.

TABLE 9. SOOT INTERACTION STUDY RESULTS[(a)]
(mg/FILTER)

Exposure Conditions	NO_3^-	NH_4^+
Filter before exposure	0.008	<0.003
11.5 ppm NH_3	0.010	<0.005
19.5 ppm NO_2	0.017	<0.003

(a) Filter medium used was Gelman A with 4-mg carbon-black loaded on a 142-mm circle.

EFFECT OF SAMPLING RATE

To examine the effect of sampling rate on nitrate collection efficiency and artifact nitrate formation, ambient Columbus aerosol was collected simultaneously over 24 hours on two groups of four Gelman AE 142-mm filters, each at two flowrates. The results of this study are included in Table 10. The average nitrate collected on the four filters run at 38.2 ℓ/min flow rate was 2.65 ± 0.16, $\mu g/m^3$ while the average for the 99.3 ℓ/min rate was 2.45 ± 0.20 $\mu g/m^3$. Since this difference is not statistically significant, nitrate collection is not affected by moderate variation of sampling rate. However, since the variation in face velocity was small (4-10 cm/sec) and even the highest, 10 cm/sec, is considerably less than a typical Hi Vol (∿50 cm/sec), extrapolation of these results to higher flow rates may not be justified.

TABLE 10. SAMPLING RATE STUDY (μg/FILTER)

Filter Material	NO_3^-	NH_4^+	Total N	m^3	$\frac{\mu g/NO_3^-}{m^3}$
Gelman AE (1)	138	29	70	56	2.46
" " (2)	380	82	160	142	2.86
Gelman AE (3)	146	29	70	54	2.70
" " (4)	360	89	170	150	2.40
Gelman AE (5)	153	42	70	54	2.83
" " (6)	315	97	200	143	2.20
Gelman AE (7)	146	29	70	56	2.61
" " (8)	345	124	200	137	2.52

EFFECT OF SAMPLING TIME

The effect of sampling time has been examined by simultaneous collection of atmospheric aerosol samples on parallel samplers. During the collections, the sample stream was split in half, with each half passing through an identical set of three filter types. One set of filters continuously sampled the atmosphere for a 48-hour period, while the second set of filters was changed after the first 24 hours of the sampling period. Comparison of the amount of nitrate collected by the 48-hour filter with the sum of nitrate collected by the two 24-hour filters will indicate whether sampling time affects the collection of particulate nitrate. The three filter types included quartz tissue (ADL), glass fiber (Gelman AE), and a compound filter consisting of a quartz (ADL) and a nylon (Duralon) filter inserted in the same filter holder. This dual filter was used to investigate whether particulate and gas-phase nitrate could be separated and determined simultaneously by a filtration technique. The quartz filter has been shown to remove particulate nitrate but not gaseous nitrate, while the nylon filter quantitatively removes gaseous nitric acid. Thus the dual filter might make the simultaneous separation and determination of the two nitrate types feasible.

The results of the total mass determinations and the aerosol nitrogen analyses for these experiments are presented in Table 11. If sampling time has no effect on the aerosol collection, then the sum of the two 24-hour filter collections should approximate the 48-hour filter sample. The data in Table 10 indicates that within the estimated experimental uncertanity, the total mass, NH_4^+, NO_3^-, and total nitrogen values are the same (no sampling time effect) for the 48-hour versus 24-hour comparisons, with two possible exceptions. The total mass collected by the two 24-hour glass-fiber filters is considerably greater than the 48-hour filter mass. We suspect a weighing error has caused this discrepancy. In addition, the 48-hour glass filter collected more nitrate than the two 24-hour glass filters. This discrepancy cannot be readily explained but is not significant enough to cause great concern.

TABLE 11. RESULTS OF THE SAMPLING TIME STUDY

	Filter Type	Total Mass, mg	NH_4^+, mg	NO_3^-, mg	Total N, mg
48-hour filter	Quartz	23.53	1.11	0.56	0.97
Sum of 24-hour filters		26.44	1.21	0.64	1.30
48-hour filter	Glass Fiber (Gelman AE)	27.92	0.74	1.92	0.85
Sum of 24-hour filters		35.03	0.93	1.44	0.94
48-hour filter	Quartz and Nylon	30.63	1.91	1.24	0.94(a)
Sum of 24-hour filters		30.03	2.11	1.28	1.08(b)

(a) Total nitrogen values for quartz filter only.

Of major interest is the fact that the glass-fiber filters collected much more nitrate than the quartz filters, almost four times as much for the 48-hour filters. This additional nitrate must be artificial and result from collection of gaseous nitrogen compounds on the alkaline glass surface. These actual atmospheric data tend to confirm our laboratory results and show the potential impact of artifact nitrate formation on glass filters.

The glass filters collected less NH_4^+ than either the quartz or the quartz + nylon. This is understandable in the case of the dual filter, since nylon was shown earlier to collect some NH_3 as NH_4^+. The lower levels of NH_4^+ collected on glass as opposed to quartz may be due to the alkaline nature of the glass filter. Such filters may tend to reject alkaline substances such as NH_3 or NH_4^+ compounds.

Table 12 shows the analyses of the individual quartz and nylon filters which made up our compound filter. Again, the sum of the 24-hour filters compared to the 48-hour filters indicates no dramatic sampling time effect. The quartz prefilter results from Table 11 compare quite well with the single quartz filter results shown in Table 10, serving as a check of our precision. The observation of NH_4^+ and NO_3^- on the nylon backup filter indicates that gaseous ammonium and nitrate precursors are penetrating the quartz filter and are adsorbed by the nylon backup. Thus, both the nylon and the glass-fiber filters suggest that a gaseous nitrate precursor can strongly influence the apparent particulate nitrate concentrations. This is completely consistent with our earlier Phase I experimental findings. It is interesting to note that the sum of the artifact nitrate collected on the nylon backup filters and the (assumed) actual particulate nitrate collected by the quartz filters is 1.44 ng for both the 48 and 24 hour filters. This is the same amount of nitrate collected by the 24-hour glass filters. While one experiment is not definitive, it does appear that the glass filter collected all the true particulate nitrate observed on the quartz filter and all the artifact nitrate collected on the nylon backup filter.

TABLE 12. COMPOUND FILTER RESULTS

	Filter Type	NH_4^+, mg	NO_3^-, mg	Total N, mg
48-hour filter	Quartz (compound)	1.11	0.36	0.94
Sum of 24-hour filters		1.13	0.48	1.08
48-hour filter	Nylon (Backup)	0.80	0.88	-
Sum of 24-hour filters		0.98	0.80	-

EFFECT OF FILTER STORAGE

Filters collected in the field for particulate nitrate determination must frequently be stored for days, weeks, or even months before the actual analyses are performed. The effect of this storage period on particulate nitrate is uncertain. Therefore, a brief investigation of storage-time effects was added to the Phase I effort.

The results of several storage-time experiments are shown in Table 13. The filters were analyzed, stored for either 2 or 7 months in

TABLE 13. RESULTS OF THE STORAGE-TIME STUDY

Filter Materials	NO_3^- Before Storage	NO_3^- After Storage	Storage Time, Mos.
Gelman AE	0.26	0.31	2
Celotate	0.047	0.016	2
Quartz (Pallflex QAST)	0.12	0.14	2
Duralon (Two 24-hr collections)	0.80	0.68	7
Duralon (One 48-hr collection)	0.88	0.69	7

glassine envelopes within sealed plastic bags, and then reanalyzed. There does not appear to be any decay of nitrate on Gelman AE or Pallflex quartz (QAST) during a 2-month storage period. Loss of nitrate from the Celotate filter is indicated; however, the precision of the analysis at such low levels is not good. This may account for part of the apparent decay. A loss of nitrate was detected on the Duralon filters. This loss may be related to the longer storage of the Duralon filter samples.

The results of this brief study suggest that storage of quartz and glass (Gelman AE) filters for periods of at least 2 months prior to analysis should have a minimal effect on particulate nitrate results.

PHASE I SUMMARY

A great deal has been learned about particulate nitrate sampling during this Phase I investigation. Our studies of the interaction between gaseous nitrogen compounds and filter substrates indicate that nylon filters, cellulose acetate filters and many glass fiber filters are subject to significant particulate nitrate interference due to the formation of artifact nitrate on the filter. Teflon, polycarbonate and quartz fiber filters showed only minimal interferences from gases studied. Considering other factors such as cost, handling characteristics, pressure drop, efficiency for submicron particle collection and mass loading considerations, the quartz filters appear most appropriate for particulate nitrate sampling, especially for large sampling networks.

Studies of the possible interaction between gases or aerosols being pulled through a filter and the particles already collected on the filter indicated no major interferences, either positive or negative, with particulate nitrate determination. The interaction between NO_2 or NH_3 and soot collected on filters was also shown to result in negligible artifact nitrate formation under the conditions studied.

Sampling time and rate were investigated in this study and were found to have no effect on particulate nitrate collection over the limited range of rates and times studied. The effect on nitrate determinations of storing filter samples up to 2 months prior to analysis was found to be negligible for glass (Gelman AE) and quartz filters.

The results of this laboratory investigation will be compared with field data on many of the same filter materials in a later section of this report.

SECTION 3

PHASE II: SCREENING AND DEVELOPMENT OF NITRATE ANALYSIS METHODOLOGY

GAS SENSING ELECTRODE

Introduction

The first technique which we investigated for nitrate determination was a new gas-sensing electrode. This electrode responds to nitrite in aqueous solution. Therefore the analytical procedure which we envisioned for nitrate determination on ambient filter extracts would involve measurement of nitrite in the extract, reduction of nitrate to nitrite, followed by a second determination of total nitrite. The difference between the two measurements represents the nitrate concentration. An advantage of this method is that both NO_2^- and NO_3^- are determined on the filter extract.

The nitrate reduction is the critical step in the procedure. Many methods have been used for nitrate reduction over the years, with variable success. However, we chose to investigate the nitrate reduction/gas-sensing electrode procedure because of reports in the literature describing new highly efficient nitrate reduction techniques. It seemed that coupling the new nitrate reduction methods with the novel gas-sensing electrode procedure might yield a highly sensitive and specific analytical technique for ambient particulate nitrate.

The electrode which we employed for this investigation was a nitrogen oxide gas-sensing electrode which responds to NO_2^- in solution. The NO_x gas sensing electrode, unlike nitrate specific ion electrodes, is almost interference free. Anions, cations, common gases, sample color, turbidity and suspended solids do not interfere with the measurement. The gas-sensing electrode is also considerably more sensitive than the nitrate ion electrode.

some volatile weak acids such as formic or acetic could interfere if present at high concentrations, but this is extremely unlikely in atmospheric aerosol samples.

The electrode utilizes a hydrophobic highly permeable membrane which allows dissolved HNO_2 from the sample (formed by NO_2^- in acid solution) to diffuse into the internal filling solution until equilibrium is established. Hydrogen ions formed in the internal filling solution by dissociation of HNO_2 are measured by the internal sensing element. The electrode potential is claimed to be Nernstian with respect to HNO_2 concentration.

The procedures used over the years to reduce nitrate to nitrite generally require extremely careful control of the reaction conditions to produce reliable results, and even then the reduction efficiency is often variable. Some of the procedures are also subject to interference by chlorides and other anions. Both zinc and copperized cadmium have been used for nitrate reduction. The use of zinc dust for the reduction presents the problem that the reduction efficiency is strongly dependent on the quality of the zinc, and in addition, some fraction of the nitrate may be reduced to ammonia. For these reasons the method is considered unreliable.

Major improvements in the reduction of nitrate to nitrite have recently been reported. Our investigation of these methods coupled with the gas-sensing electrode is described below.

Experimental

The gas-sensing electrode employed for these experiments was an Orion Research Nitrogen Oxide Electrode - Model 95-46. The electrode output was monitored with a Keithley Electrometer - Model 600 A. For some experiments the output was also read with an Orion Specific Ion Electrode Meter: the results were identical. The electrode was assembled and checked out according to the instructions provided with the electrode. An immediate problem developed when the electrode displayed non-Nernstian behavior. A factor of ten variation is solution NO_2^- concentration resulted in a 50 ± 3 mv change rather than the 58-60 mv variation expected. The electrode membrane was replaced, the internal solution was changed, and new standards prepared, all without effect. Conversations with Orion personnel resulted in several additional changes and tests, all of which failed to bring the electrode response up to the proper value. Since all of the other characteristics of the electrode were in order, calibration curves were prepared and the electrode was used without further efforts to adjust the response behavior.

One type of reduction catalyst was prepared according to the method Lambert and Du Bois(22) from copper (II) sulfate, powdered cadmium, ammonium chloride and dibasic sodium phosphate. A second catalytic procedure required amalgamated cadmium in alkaline solution. Reagents employed for this procedure were mercuric chloride, cadmium powder, sodium citrate, sodium hydroxide, barium hydroxide and perchloric acid. This second catalyst and reduction procedure are described in the instruction manual for the nitrogen oxide electrode - Model 95-46, Orion Research, Cambridge, Mass. Samples and standards employed during this investigation were prepared with deionized and distilled water. Prior to each measurement with the gas-sensing electrode the sample pH was adjusted to approximately 1.2 using an acid buffer. This is required to convert nitrite ions into dissolved gaseous nitrous acid.

Results and Discussion

The objective of this phase of our program was to screen methods for nitrate analysis and, based on the results of the screening process, develop a nitrate analysis procedure which is fast, reliable, sensitive and specific. At the start of our study, the gas-sensing electrode coupled with a nitrate reduction procedure seemed to meet these criteria. During our subsequent investigation we found that the gas-sensing electrode has all of the required characteristics. It was fast (2-3 minutes per determination), reliable and sensitive to less than 0.1 ppm nitrite. The electrode is relatively free from interferences except at the lowest nitrite levels. Under conditions where highest sensitivity is required, it is recommended that the sample be pretreated to remove dissolved atmospheric CO_2.

While the gas-sensing electrode met the criteria we had established the overall analytical procedure did not. The problems with the method occurred in the nitrate reduction step. The reduction catalysts which we employed were difficult to prepare uniformly and tedious to use. The greatest problem was the slowness of the reduction step. Our initial attempts at using a reduction column showed very erratic reduction efficiencies. The efficiency was increased by using catalyst preparations of finer mesh, but at an acceptable efficiency the flow rate through the reduction column was intolerably slow. Experiments with different catalyst particle sizes and different column geometries failed to provide a reduction which was both fast and efficient.

Since the objective of this phase of our program was to screen potential nitrate analysis procedures, we also investigated a chemiluminescent and an ion chromatographic procedure simultaneously with the gas-sensing electrode. Due to the difficulties encountered with the nitrate reduction step and the positive results we were obtaining with chemiluminescence and ion chromatographic techniques, work on the gas-sensing electrode procedure was terminated in order to devote our full attentions to the latter two methods. These methods are described in the next sections of this report.

THERMAL DECOMPOSITION/CHEMILUMINESCENCE

Introduction

A method for particulate nitrate determination which theoretically seemed to possess the required criteria of speed, sensitivity and selectivity is thermal decomposition of nitrate followed by chemiluminescent detection. We envisioned a technique wherein nitrate in ambient aerosol, either on a filter substrate or dissolved in water, would be decomposed to NO_x by rapid heating. A carrier gas would then transport the NO_x to a commercial chemiluminescent nitrogen oxides monitor. The integrated output signal was expected to be proportional to the original nitrate concentration. Brief investigation of this procedure by other researchers$^{(23,24)}$ confirmed that the method seemed promising. Chemiluminescent NO_x monitors measure the light emitted (600-900 nm) when NO in the sample reacts with excess O_3. The sensitivity of commercial instruments is generally 5-10 ppb by volume of NO. Various catalytic converters are employed to reduce NO_2 (and other gaseous nitrogen compounds) to NO for determination; thus the instrument is said to monitor total NO_x. For determining NO the chemiluminescence instruments are fast, sensitive and free from interference. Our task in developing and validating a thermal decomposition/chemiluminescent method for atmospheric particulate nitrate determination involved primarily the thermal decomposition step and introduction of the gaseous decomposition products into the chemiluminescence monitor. Our results demonstrate that the procedure discussed in this report is a rapid, sensitive, selective, and relatively simple method for nitrate determination.

Experimental

Two commercial chemiluminescence instruments were employed in this investigation. The majority of the work was conducted using a Bendix Model 8101-B chemiluminescence NO/NO_x monitor. This instrument was employed in a continuous mode (as opposed to its normal cyclic operation). For most experiments the instrument's heated carbon catalytic converter was employed to reduce any NO_2 in the sample stream to NO, even though several experiments demonstrated that NO accounted for >90 percent of the nitrate decomposition products. Use of the converter ensured that even the traces of NO_2 formed in the decomposition process were meas[illegible] For some experiments a Thermo Electron Corp. Model 14-D chemiluminescence NO/NO_x monitor was used. The Model 14-D is a dual channel instrument [illegible]ich simultaneously monitors NO and NO_x. It employs a heated molybdenum catalytic converter for reduction of NO_2 to NO. Both instruments were calibrated with low concentrations (0.5-5 ppm) of NO in N_2. The calibration standards were referenced to a National Bureau of Standards "NO in N_2" primary standard. A Hewlett-Packard Model 3370 A integrator was used to integrate and digitize the instrument output.

One series of experiments employed an 18 cm by 2 cm quartz tube surrounded by a resistance heated furnace for sample decomposition. A second series used a resistance heated 18 cm by 0.30 cm stainless steel tube for sample decomposition. Two electrodes connected the loop to a stepdown transformer. The temperature of both the quartz tube and the stainless steel loop was determined with a chromel-alumel thermocouple. Teflon tubing was employed for the gas flow system. Tedlar (polyvinyl fluoride) bags were used for a number of experiments to collect and integrate the gaseous decomposition products. The stability of NO_x in these bags was excellent over the short times required.

Ambient filter samples as well as aqueous standards were frequently analyzed simultaneously by the chemiluminescence method and ion chromatography. Discussion of the ion chromatographic procedures and results will be reserved for a later section of this report.

Results and Discussion

Our investigation of the feasibility of a thermal decomposition/chemiluminescence procedure for atmospheric particulate nitrate determination suggested two different experimental configurations. The first design utilized direct injection of the gaseous decomposition products into the chemiluminescence monitor, with digital integration of the chemiluminescence signal. This method is rapid, extremely sensitive, but not highly precise.

The second experimental set-up integrates the gaseous decomposition products in a small Tedlar bag. The concentration of the products in the bag is then determined by the chemiluminescence monitor. This method is cheaper and simpler to set-up and operate but not as sensitive as the first procedure.

Many of our initial experiments to characterize the thermal decomposition process utilized the first, direct injection, method. The following section will describe one variation of the direct injection method and the results of our temperature and interference studies. Subsequent sections will discuss the bag integration technique and variations in the direct injection method.

Direct Injection--

The apparatus for the initial series of experiments consisted of a Vycor tube placed in a resistance furnace with a 450°C maximum temperature. The inlet of the Bendix chemiluminescence monitor was connected directly to the Vycor tube by Teflon tubing, so that room air was drawn through the heated tube and directly into the monitor. The sampling pump of the Bendix monitor pulled air through the system at approximately 120 cc/minute. The monitor was operated in the continuous NO_x mode and the signal routed to the digital integrator.

In the initial experiments small quantities of nitrate compounds were introduced into the hot zone of the Vycor tube using either platinum or Vycor boats. For most experiments 1-50 μl of aqueous sample were placed in the boat, dried by evaporation at the entrance to the Vycor furnace tube, and finally inserted into the hot zone of the furnace with Vycor rod.

Using the platinum boat, this procedure had a detection limit of less than 1 μg NO_3^-; however the Pt boat blank was equivalent to about 0.2 μg NO_3^-. Vycor boats were employed with the same result. These blank values need to be reduced substantially in order to obtain the required sensitivity. Different methods of washing, baking and flaming the boats were tried in order to reduce the blanks. These methods were successful if the boats were used immediately after cleaning. However, a few minutes exposure to room air resulted in high blanks again. It appears that NO_x from room air is adsorbed at the platinum or Vycor surface. This NO_x then desorbs and interferes with the NO_3^- determination when the boat is injected into the furnace. This same phenomenon was observed when a Vycor rod was used to insert and withdraw the boats from the furnace hot zone. The problem with the rod was easily overcome by leaving the rod in the furnace continuously.

Before concentrating on the blank problem, we investigated the other characteristics of the apparatus to ascertain the feasibility of the thermal desorption/chemiluminescence method. Using the Vycor boat, quantities of $NaNO_3$ standards equivalent to 0.1, 0.2, and 0.5 μg of NO_3^- were flashed in the furnace and the resulting NO_x determined by chemiluminescence. To extend the calibration curve to even lower values, injections of dilute NO gas equivalent to 4, 8, 21, and 41 ng NO_3^- were performed with a gas-tight syringe. A log-log plot of peak area vs μg NO_3^- yielded a straight line and suggested that a detection limit of less than 10 ng might be possible if interference and blank problems could be overcome. The results obtained with this crude furnace apparatus confirmed that the method was promising. Subsequent experiments were designed to optimize, simplify and validate the method.

Reduction of Blank Values--

Since the results obtained with the crude experimental apparatus appeared promising, we investigated different ways of lowering the high blank values associated with the Vycor and platinum boats. As a first step toward improving the procedure we replaced the Vycor tube and furnace with a heated gas chromatographic injector port. G.C. injector systems are employed routinely to flash microliter volumes of sample into a carrier gas stream. The small volume of the injector should deliver the decomposition products to the chemiluminescent analyzer in a very sharp pulse, which would lead to an improvement in minimum detectability limits. A nitrogen carrier gas was used in our system to purge the injector port and carry the decomposition products to the chemiluminescent monitor. Nitrogen carrier gas was used to minimize the potential interference of NH_4^+ on the NO_3^- determination, since the removal of O_2 from the system should inhibit the conversion of NH_4^+ to NO_x in the hot zone. Liquid syringes were used to inject the sample through the septum and into the hot zone, thus avoiding the use of sample boats. A special convection cooled extension was fitted to the injector to maintain the septum temperature at <200°C while the hot zone exceeded 425°C.

Results using the G.C. injector port for thermal decomposition of aqueous nitrate samples were highly scattered. It appeared that the high temperatures required for decomposition of nitrate salts prevented reproducible injections. The water apparently evaporated from the syringe needle before the injection was complete, leaving nitrate salt deposites to decompose in the needle rather than in the injector port. A number of modifications to the procedure were attempted, but none improved the reproducibility to an acceptable level.

Because of the negative results with the injector port, the apparatus was reassembled in its original Vycor furnace tube configuration, and alternatives to the Vycor and platinum boats were sought. After considerable investigation the sample vessel which showed the lowest blank was found to be small (∿4 mm diameter) circles of high purity quartz fiber filter material used in our ambient filter sampling experiments. The filter vehicles are prepared by punching out a portion of a quartz filter with a No. 2 cork borer.

This provides a filter circle 4.3 mm in diameter with 0.15 cm^2 area. For ambient filter samples, such small pieces may be analyzed directly by flashing in the furnace, or a known volume of aqueous filter extract can be syringed onto a clean filter pad prior to flashing. The lower detectable limit for NO_3^- using this procedure is below 10 ng due to the low and reproducible nitrate blank of the filter pads.

A series of experiments was undertaken to document the reproducibility of the filter pad injection technique. Microliter volumes of aqueous nitrate standards were syringed onto filter pads and subsequently flashed and analyzed. The peak area was then used to determine the relative standard deviation at each nitrate concentration. For these initial tests a concentration range from 100-2000 ng NO_3^- was employed. The relative standard deviation of multiple determinations (4-6) was 10-15 percent. More detailed reproducibility studies were postponed pending further refinement and characterization of the method. The next step in characterizing the procedure involved an investigation of interferences.

Interferences--

The likely interferences with this procedure are nitrite, ammonium, and possibly organic nitrogen compounds which can decompose to NO_x.

Experiments with $NaNO_3$ and NH_4NO_3 solutions demonstrated that ammonium interferes with the determination of NO_3^-. The ammonium presumably decomposes in the presence of oxygen in the 425°C furnace to yield NO_x. To eliminate the NH_4^+ interference the Vycor furnace tube was connected via a ball joint and Teflon tubing to a gas cylinder of oxygen-free nitrogen. The Vycor tube was connected to the N_2 source via a tee which was extended and tapered to permit access to the furnace for the Vycor rod. A continuous flow of excess N_2 passed out of the open end of the tee, thereby excluding room air from the furnace.

Experiments were then conducted with both NH_4Cl and NH_4NO_3 solutions to determine the extent of NH_4^+ interference in the absence of O_2. The results demonstrate that the NH_4^+ interference is almost totally eliminated by decomposing the sample in a nitrogen atmosphere. For example, the response of 100 ng NH_4^+ in NH_4Cl produced an equivalent NO_3^- response of less than 4 ng. Amines and other organic nitrogen compounds, which may be present in atmospheric filter samples at very low concentrations, were investigated in several experiments; no significant interference was observed as long as O_2 was excluded from the decomposition tube.

Interference due to decomposition of nitrite salts is essentially quantitative, as expected. We do not believe that nitrite interference is a serious problem in the analysis of ambient filter samples however, because of the low levels of nitrites present in ambient aerosol samples. For example, our studies in several U.S. cities have shown(16) that particulate nitrite averages 1-2 percent of the particulate nitrate concentration. Thus nitrite interference should be minimal for ambient particulate analysis.

Calibration--

In theory, calibration of the chemiluminescent instrument with known concentrations of NO or NO_2, as is done when the instrument is used for continuous monitoring, should also be sufficient for determining nitrate if the decomposition and transfer to the monitor is quantitative. To determine whether this is the case, and also to check the linearity of the system, a standard calibration curve was prepared using aqueous solutions of $NaNO_3$. Our initial attempt to prepare such a curve demonstrated that the response time of the instrument was insufficient to efficiently monitor the tall sharp peaks resulting from high concentrations of nitrate. This problem was overcome to a great extent by inserting a 200 ml pyrex ballast vessel between the Vycor furnace and the chemiluminescence monitor. This vessel served to lower and broaden the peak, thereby improving the peak area measurement. Subsequent sections of this report will describe other means of overcoming the response time problem.

Using the system incorporating the ballast, a calibration curve was prepared with $NaNO_3$ standards. Twenty-six points were used to derive the curve shown in Figure 10. The best fit equation of the line shown in the figure is

$$[NO_3^-] = 5.98(\text{Peak Area})^{1.05}$$

with $[NO_3^-]$ in ng and peak area in volt-seconds. The theoretical response

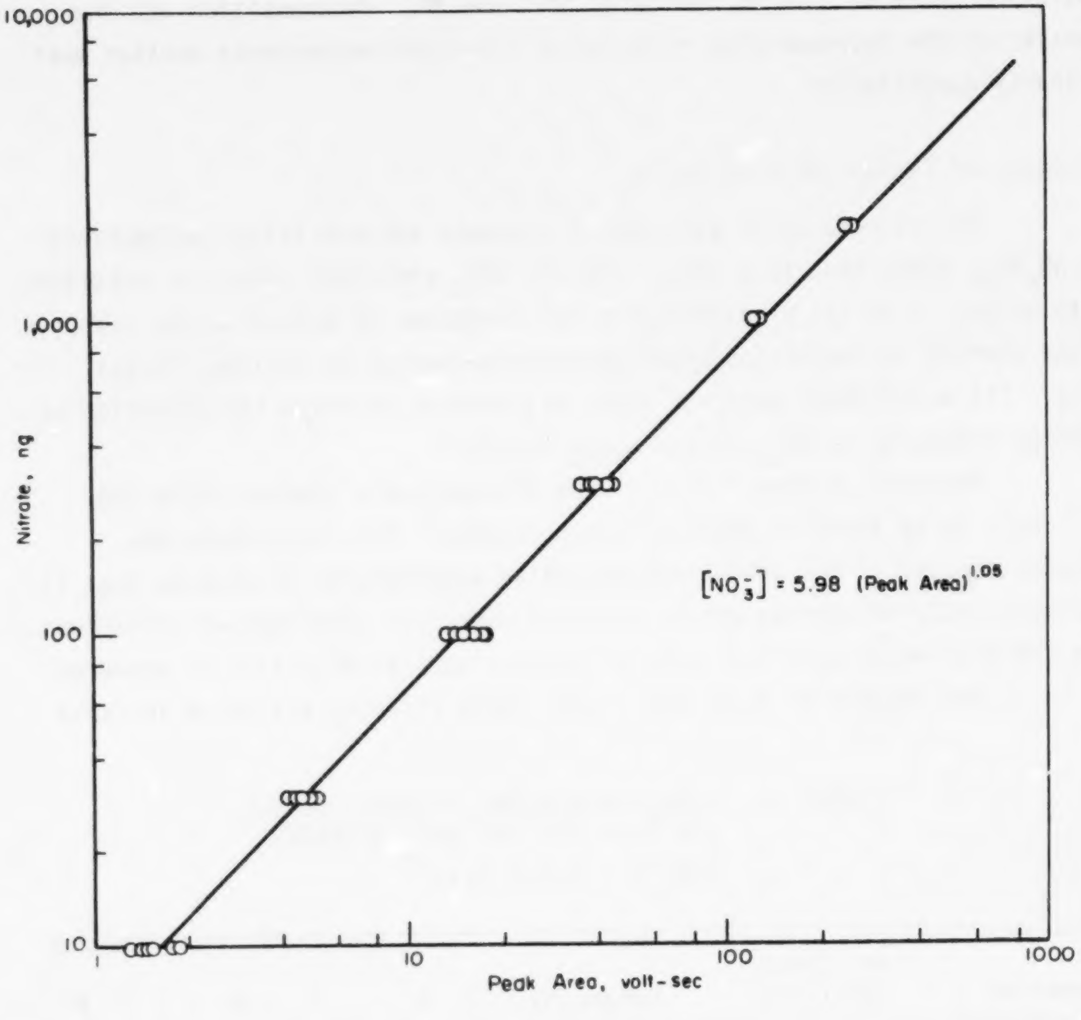


Figure 10. Calibration curve for the chemiluminescence technique.

curve equation at 25°C and 750 mm Hg is

$$[NO_3^-] = 5.93(\text{Peak Area})^{1.00}$$

The agreement between the theoretical and measured responses over the concentration range we studied indicates that the NO_3^- decomposition and the transfer of the decomposition products to the chemiluminescence monitor must be nearly quantitative

Responses of Various Nitrate Salts--

The nitrate salts expected to dominate ambient filter collections are NH_4NO_3, $NaNO_3$ and, to a lesser extent, KNO_3 and other alkali or alkaline-earth salts. A series of experiments was conducted to determine the response of the thermal decomposition/chemiluminescence method to various nitrate salts. All experiments were run under nitrogen to minimize the oxidation of ammonium compounds to NO_x, as discussed earlier.

Ammonium, sodium and potassium nitrates were studied since they are likely to be found in ambient filter samples. Calcium nitrate was selected because it has a high decomposition temperature; we presume that if calcium nitrate decomposes and is measured under our experimental conditions, then the vast majority of nitrates in ambient samples will also be measured.

The results of experiments with these nitrates are shown in Table 14.

TABLE 14. CHEMILUMINESCENCE RESPONSE CURVES FOR SELECTED INORGANIC NITRATES

$[NO_3^-] = A[\text{Peak Area}]^B$

Compound	No. Samples Analyzed	Range, ng	A	B	R
$NaNO_3$	7	20-2000	1.46±.03	1.11±.01	0.99
NH_4NO_3	7	20-2000	1.63±.03	1.08±.01	0.99
KNO_3	7	20-2000	1.42±.09	1.12±.02	0.99
$Ca(NO_3)_2 \cdot 4H_2O$	6	100-4000	1.13±.05	1.13±.01	0.99
Theoretical			1.84	1.00	

Included in the table are the coefficients, exponents and correlation coefficients of logarithmic plots of nitrate concentration versus chemiluminescent response (peak area). The theoretical exponent and coefficient values for our experimental conditions are also tabulated. In all cases, the exponent is greater and the coefficient less than theoretical. These deviations counteract one another to a great extent, except for $Ca(NO_3)_2$. In all other cases, the error involved in using one of the exponent/coefficient combinations rather than another is small. For most applications we suggest using NH_4NO_3 for calibraiton since this is the most likely nitrate salt in ambient samples. The curve resulting from the NH_4NO_3 data was also closest to the theoretical curve.

The calcium nitrate results suggest incomplete decomposition, with ∿70 percent recovery at the low end of the concentration range and higher recoveries at higher concentrations. Since the nitrates expected to be present in ambient samples are nearly completely recovered, and even a salt with such a high decomposition temperature as $Ca(NO_3)_2$ is largely recovered under our experimental conditions, we can be confident of nearly quantitative nitrate recovery from ambient particulate samples.

Filter Sample Homogeneity--

As mentioned earlier, two procedures are available for analysis of filter samples using the thermal desorption/chemiluminescence system. A known volume of the aqueous filter extract can be injected into the furnace hot zone on a clean quartz filter pad, or a small portion of the actual filter sample can be flashed in the furnace directly, thereby eliminating the extraction step. To demonstrate the utility of this latter procedure, 4 mm diameter circles were cut from three different 142 mm filters used to collect aerosol in Columbus, Ohio. The results of the chemiluminescent analyses are shown in Table 15 as micrograms of nitrate on the filter. Two samples each were taken from the edge and the center of each filter. The reproducibility between samples taken from the same portion of the filter is reasonable. However, the data strongly suggest a concentration gradient from the center to the edges of the filter. The filter holder used to collect the aerosol samples was conical, so that one might well expect a concentration gradient based on aerodynamic effects. While other common

TABLE 15. CHEMILUMINESCENT NITRATE METHOD REPRODUCIBILITY STUDY USING AMBIENT AEROSOL

Filter Material	Region	μg NO_3^-
Pallflex QAST	Edge	551
" "	"	569
" "	Center	853
" "	"	942
Gelman AE (Port #1)	Edge	3650
" "	"	3530
" "	Center	>3930(a)
" "	"	>4160(a)
Gelman AE (Port #2)	Edge	2980
" "	"	2930
" "	Center	4270
" "	"	4160

(a) Integrator saturated. Minimum value shown.

filter sampler designs may not result in such serious concentration gradients, still we have conducted the remainder of our experiments on filter extracts in order to eliminate this potential source of error.

At this point we reviewed our progress on the thermal decomposition/chemiluminescence method, with the aim of simplifying and optimizing the procedure. This review led to some rather significant modifications to the procedure, described in the following section.

Simplification of the Thermal Decomposition/Chemiluminescence Apparatus and Procedures--

Our review of the apparatus and procedures suggested several modifications which would greatly simplify the analysis and substantially reduce the cost of the apparatus. During the studies just described, we had also noticed occasional reproducibility problems relating to the time constant of the chemiluminescence monitor. During the thermal decomposition of the nitrate, a pulse of NO_x is sent to the chemiluminescence monitor. It appeared that the monitor did not always respond rapidly enough to this pulse, so that not all of the NO_x was integrated. Our initial attempts to overcome this problem made use of a ballast to spread out the NO_x peak before it entered the NO_x monitor. However, because of the extreme sensitivity of the technique, even small portions of ambient filter samples tended to overload the system, as seen in Table 15 presented earlier. We have solved these problems and also greatly simplified the technique by collecting and diluting the pulse of NO_x in a Tedlar bag. The bag serves to integrate the sample so that the costly and complex digital integrator is eliminated from the system.

In practice a liquid sample is injected into a stainless steel loop, An evacuated Tedlar bag is connected to the system and nitrogen flow is started through the loop and into the bag. At this point the loop is heated rapidly to 425°C via two electrodes connected to a stepdown transformer. The NO_3^- decomposes rapidly and the NO_x is carried into the bag by the N_2 flow. The N_2 flow is continued for 1-2 minutes to insure that all the NO_x has been collected; total volume collected in the bag is 1000-1500 ml. The bag is then connected to the chemiluminescence monitor and the NO_x concentration determined. This concentration along with the N_2 volume is used to calculate the original NO_3^- concentration. The entire analysis require

7 minutes. By continuing to dilute the NO_x collected in the bag, the upper limit of the technique can be extended almost indefinitely. Since the decomposition temperature is the same as in the original apparatus and N_2 is again used as carrier gas, the previous results on recovery efficiencies and interferences should still be valid

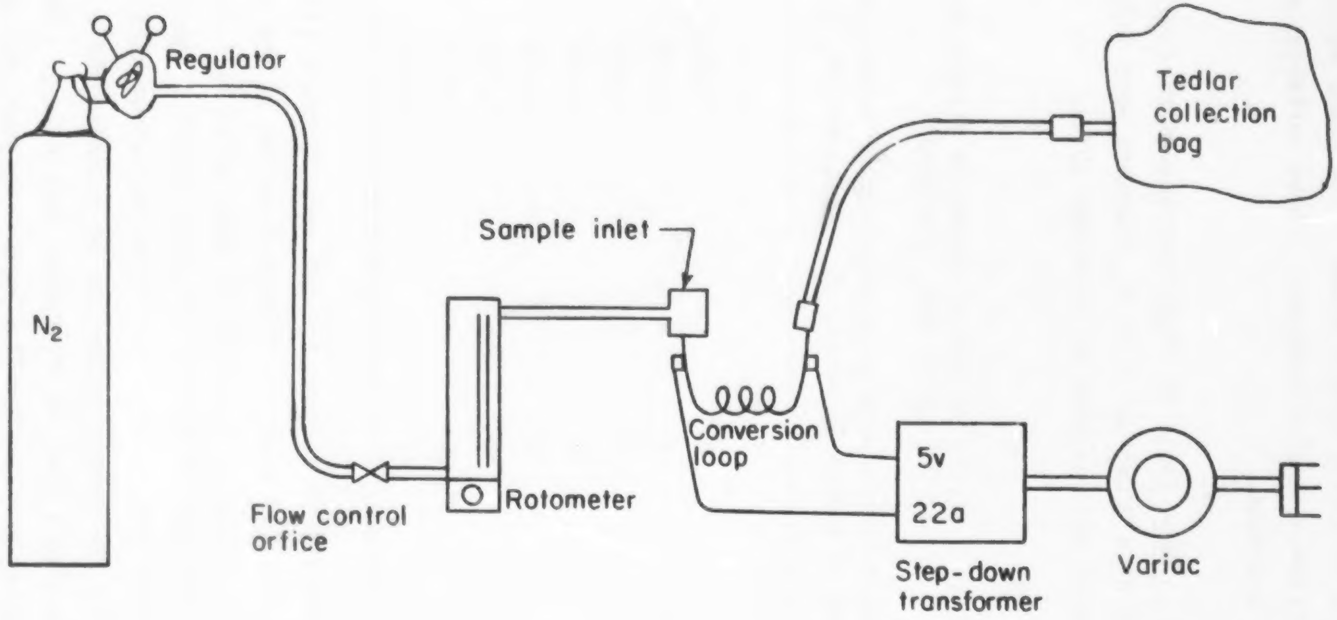
The importance of the simplifications described here should be emphasized. The chemiluminescence apparatus can now be assembled in a few hours and operated easily by laboratory technicians. The cost of the apparatus and the time per determination have been significantly reduced. These advantages come at a cost in sensitivity. However, the modified technique still has sufficient sensitivity for ambient filter analysis. A detailed description of the modified apparatus is given below.

Description of the Modified Apparatus--

A schematic of the modified thermal decomposition/chemiluminescence apparatus is shown in Figure 11.

The apparatus is used to decompose NO_3^- to NO_x by heating a liquid sample to >400°C inside of a loop of 1/8" stainless steel tubing. The heat is generated by passing a 5 volt, high amperage current through the metal loop. The temperature is regulated by connecting the step-down transformer to a Variac. A thermocouple is positioned at the site of sample injection. Nitrogen, used as the carrier and dilution gas, is passed through the conversion loop and into a Tedlar collection bag. The flow rate is regulated to obtain the desired dilution of the sample.

The conversion loop was made by wrapping 1/8" stainless steel tubing twice around a 1/2" diameter rod. Electrodes from the transformer were placed on either side of the coil. A swagelok tee fitting was installed on one end of the loop with a septum for sample injection. A non-conductive type ferrule must be used to insure that the conversion loop is electrically isolated from ground. Stainless steel fittings and Teflon tubing are used between the loop outlet and the collection bag to minimize NO_x adsorption. Quick connect fittings are utilized to facilitate the rapid transfer of the bag to the NO_x analyzer.



Regulator
N_2
Flow control orfice
Rotometer
Sample inlet
Conversion loop
Tedlar collection bag
5v
22a
Step-down transformer
Variac

Figure 11. Thermal decomposition apparatus.

Characteristics of the Modified Apparatus--

While the apparatus pictured in Figure 11 is conceptually simple, several variables, including sample volume, flow rate, accuracy and precision must be optimized and/or assessed. These variables are discussed in the following sections.

Sample volume--Table 16 shows the results of sample volume studies. Different volumes of a 0.099 μg/μl Na NO_3 standard were injected into the sample loop, flashed and analyzed as described above.

TABLE 16. EFFECT OF SAMPLE VOLUME ON NITRATE ANALYSIS (0.099 μg/μl $NaNO_3$ standard)

Volume of Sample Injected, μl	Measured $[NO_3^-]$, μg/μl
1	0.113
2	0.084
4	0.088
7	0.096
10	0.094
15	0.098
20	0.093
25	0.077
40	0.061

The 1 and 2μl injections are not very accurate since the background NO_x in the N_2 carrier gas makes up a large fraction of the total measured NO_x at such low sample volumes. Injection volumes which fall in the range 4-20 μl yield reproducible and reasonably accurate results. Above 20μl the recovery of NO_x falls off. Additional tests not shown here demonstrate that the upper limit for the sample volume can be extended above 20μl by increasing the sample residence time in the heated sample loop. This is accomplished easily by reducing the carrier flow rate. However, for most purposes a

10-15μl injection volume should be entirely sufficient. As an example of the accuracy and precision of the method, seven 15μl injections of the 0.099μg/μl $NaNO_3$ solution were run. These samples yield an average nitrate of 0.098±0.005μg/μl.

Flow rate--The flow rate of N_2 through the injection loop and into the Tedlar collection bag is constrained in two ways. First, the flow must be kept low enough that it does not blow the liquid sample through the loop. Secondly, the flow should be optimized so that the total volume of sample in the Tedlar bag is sufficient for chemiluminescence analysis but not so great as to excessively dilute the NO_x decomposition products. In practice we found a flow rate of about 200 ml/min and a total volume of 1.0-1.5 liters to be ideal for our system. Operationally, the following procedure yielded the most reproducible results:

(1) Inject sample into the conversion loop
(2) Initiate N_2 flow through loop and into collection bag
(3) After 30 seconds apply heating current to loop
(4) Discontinue both flow and heat 5 minutes after flow was started
(5) Disconnect collection bag from loop and connect to chemiluminescence monitor. Read the NO_x concentration after the signal becomes steady.
(6) Allow loop to cool below 100°C before injecting another sample (this can be done rapidly by squirting water on the loop)
(7) Periodically determine the system blank by analyzing the pure water used for filter extractions in the same manner as above.

Accuracy and precision with various nitrates--To further characterize the refined thermal decomposition/chemiluminescence procedure, aqueous solutions of three different nitrate salts were prepared and analyzed by ion chromatography and chemiluminescence. The results of these analyses are shown in Table 17. Discussion of ion chromatography is reserved for a later section of this report. However, the agreement between chemiluminescence method and ion chromatography is quite good. Both instruments were calibrated independently. The chemiluminescence results are 3-5 percent lower than the ion chromatographic data. This small discrepancy could have resulted from small errors in preparing calibration standards for one or the other instrument. Based on the data in Table 17, there are clearly no significant differences in the extent of decomposition among these three salts.

The relative standard deviation for the chemiluminescence results varies from 2 percent for sodium and potassium samples to 4 percent for the NH_4NO_3 solution. These deviations are based on 3-5 replicates for each solution.

Since the preliminary experiments with the refined thermal decomposition/chemiluminescence method seemed promising, a more detailed set of comparisons was carried out using NH_4NO_3, KNO_3, and an actual ambient filter extract. Solutions of NH_4NO_3 and KNO_3 were perpared at 5, 50 and 550 ppm (μg/ml) and analyzed in quadruplicate by both ion chromatography and chemiluminescence. The aqueous extract from a high volume filter collected on October 19, 1976, during our Phase III field study (to be discussed later in this report) was also analyzed by both methods. The results of these experiments are presented in Table 18.

Referring to the data in Table 18, the following points can be made.

(1) The I.C. results are consistently 3-7 percent below the prepared sample concentrations. The chemiluminescence results are less consistent, but in four out of six cases the chemiluminescent results are closer to the true concentration than I.C.

TABLE 17. COMPARISON OF CHEMILUMINESCENCE WITH ION CHROMATOGRAPHIC NITRATE DETERMINATIONS

Compound	Ion Chromatograph µg NO_3^-	Chemiluminescence* µg NO_3^-
$NaNO_3$	2.97	2.82 ± 0.06
KNO_3	2.89	2.79 ± 0.06
KNO_3	1.93	1.86 ± 0.04
NH_4NO_3	2.80	2.73 ± 0.11

* 3-5 replicates

TABLE 18. REPLICATE NITRATE ANALYSES

Sample (Concentration for NO_3^-)	Ion Chromatographic Method	Chemiluminescent Method
	NO_3^-, ppm	NO_3^-, ppm
5 ppm NH_4NO_3	4.6	5
	4.5	5
	4.6	5
	4.6	6
	4.6 ± 0.1	5 ± 1
50 ppm NH_4NO_3	46.2	54
	46.0	50
	46.5	49
	46.6	50
	46.3 ± 0.3	51 ± 2
500 ppm NH_4NO_3	464	505
	464	519
	464	495
	468	466
	465 ± 2	496 ± 22
5 ppm KNO_3	4.6	5
	4.6	3
	4.6	4
	4.6	4
	4.6 ± 0.0	4 ± 1
50 ppm KNO_3	48.5	50
	48.8	50
	48.8	48
	48.8	50
	48.7 ± 0.2	50 ± 1
500 ppm KNO_3	477	466
	477	485
	479	452
	479	476
	478 ± 1	470 ± 14
Los Angeles Filter - 10/19/76	131	126
	134	132
	132	138
	132	132
	132	139
	132 ± 1	133 ± 5

(2) The reproducibility of the ion chromatograph is considerably better than the chemiluminescence procedure, especially at low concentrations. This is due primarily to the fact that milliliter amounts of sample are injected into the I.C. while microliter samples are employed in the chemiluminescence procedure. The relative standard deviation of the I.C. data is better than 1 percent in all cases but one. The relative standard deviation of the chemiluminescence results is better than 4 percent for all cases except the two low-concentration samples. A 20-25 percent deviation is observed for those samples. Since those two samples are based on injection of only 50 ng of nitrate into the chemiluminescence system, the imprecision is perhaps understandable. In the case of such low concentrations, the direct injection thermal decomposition/chemiluminescence system will provide much greater sensitivity and precision.

(3) The average nitrate value for the Los Angeles filter sample as determined by chemiluminescence is quite similar to the ion chromatographic result.

Comparison With Ambient Filter Samples--

As a final test of the refined thermal decomposition/chemiluminescence method, filter extracts from 17 high volume filters were analyzed simultaneously by ion chromatography and chemiluminescence. These filter samples were collected for 8 hours (0900-1700 PDT) a day at two sites in the Los Angeles basin. The results of these analyses are plotted in Figure 12. The "equivalent response" line has also been drawn in the figure. It seems clear that, over the range of nitrate concentrations represented by these actual ambient filter collections (i.e., 0.3-52 $\mu g/m^3$), the chemiluminescence and ion chromatographic methods yield similar results. Since ambient nitrate concentrations will rarely fall outside this concentration range, these results confirm the utility of the thermal decomposition/chemiluminescence method for ambient particulate nitrate determination.

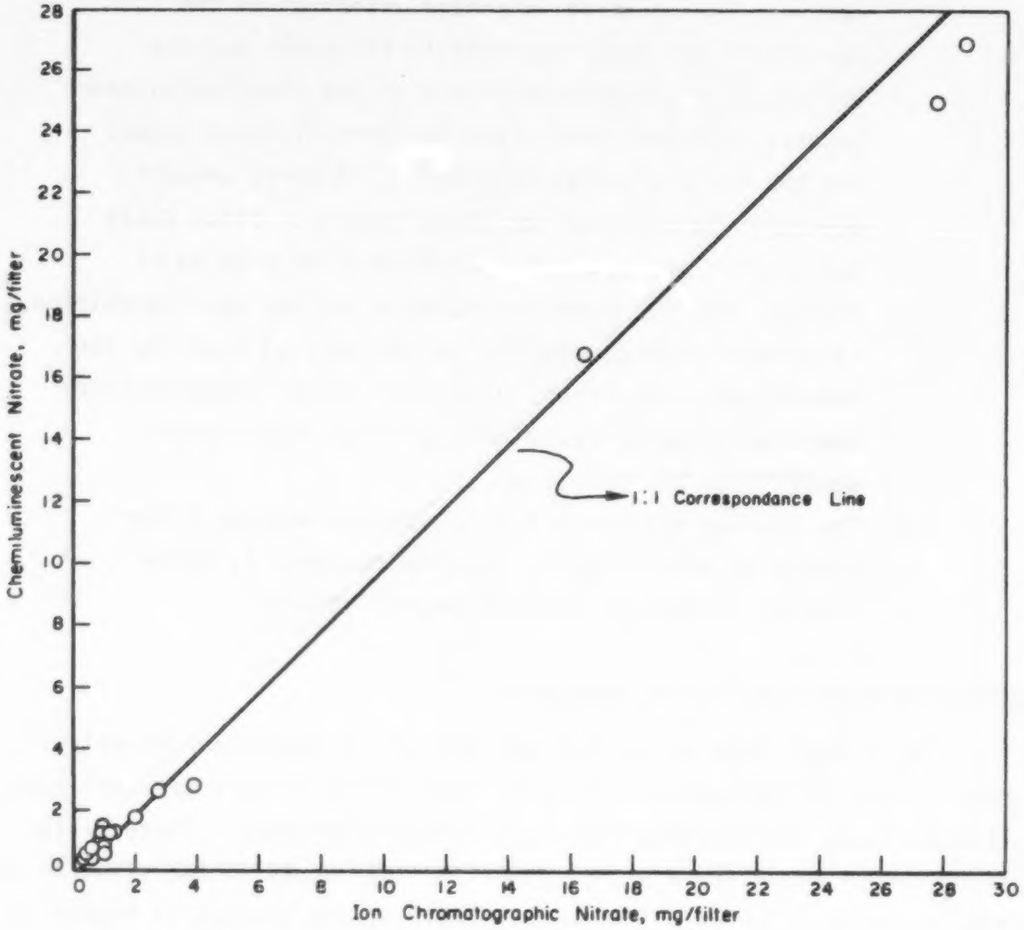


Figure 12. Comparison of chemiluminescent and ion chromatographic methods for ambient filter samples.

Direct Injection with Modified Apparatus--

As a final step in our investigation of thermal decomposition coupled with chemiluminescence to determine nitrate in atmospheric particulate samples, we have studied the direct injection of sample decomposition products into the chemiluminescence monitor. Our earlier studies of direct injection showed some irreproducibility, especially at high concentrations, due to a chemiluminescence response time which was too slow to quantitatively detect the sharp pulse of NO_x which results from the thermal decomposition. In reinvestigating direct injection we employed a TECO 14D chemiluminescence monitor and the modified decomposition apparatus described in the previous section. The TECO 14D has a much higher flow rate ($\sim$1 lpm) and more rapid response than the instrument employed for the initial direct injection experiments.

Results of the direct injection experiments with the TECO 14D are shown in Figure 13. A 0.5μl sample volume was used for these experiments. Digital integration was employed for peak area determination. The data points are scattered about the theoretical line, showing good linearity. Linear response up to 1000 ppm NO_3^- has been observed. The technique can detect about 3 ng NO_3^- in a 15μl sample; approximately 30 samples can be analyzed in an hour. With this sensitivity, even the lowest rural Hi Vol filter nitrate concentrations can be determined.

ION CHROMATOGRAPHY

Shortly after our investigation of the thermal decomposition/chemiluminescence procedure was initiated, a new analytical technique was introduced to the atmospheric analysis community. The technique was called ion chromatography. To evaluate the utility of this new technique for atmospheric particulate nitrate determination, our original contract was extended by several months. During this time several reports and much data have accumulated on the use of ion chromatography for atmospheric particulate analysis. In this section of the report we will briefly review these studies and describe our investigations of this new technique for ambient particulate nitrate determination.

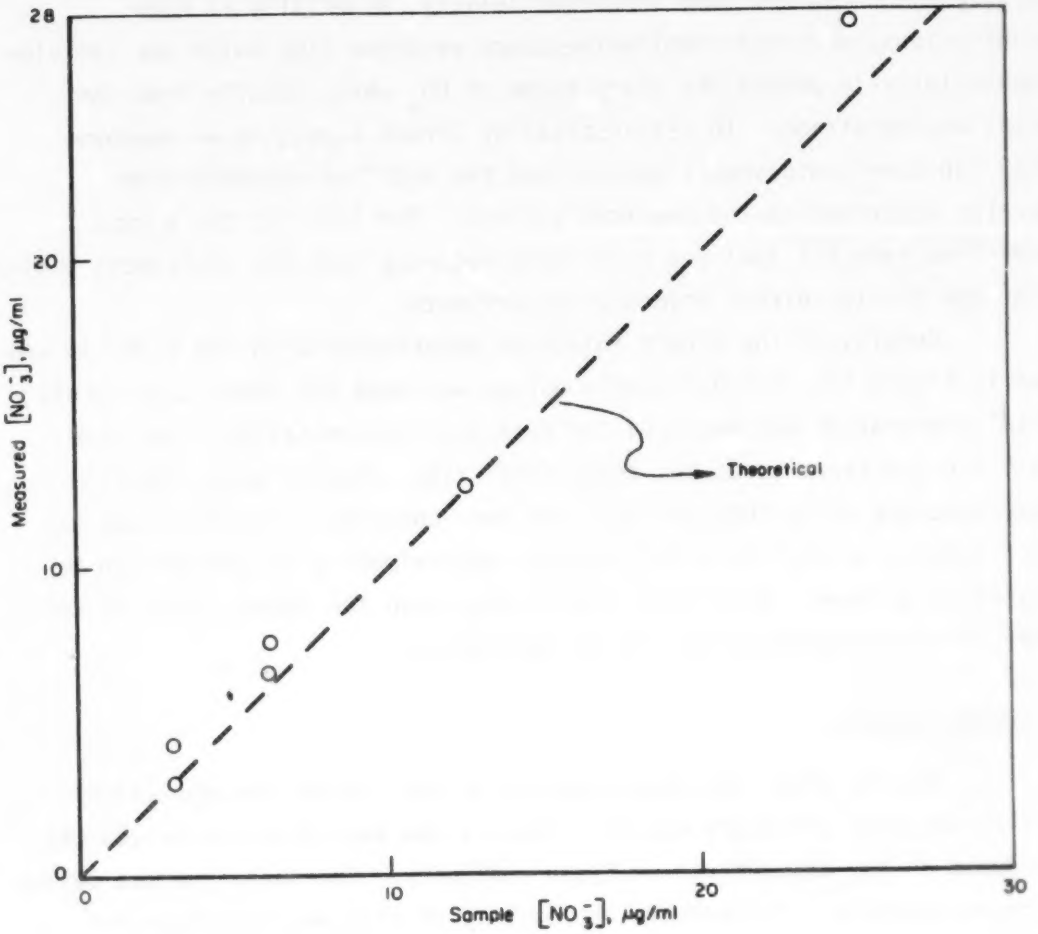


Figure 13. Results of direct injection experiments

Background

The technique now referred to as "ion chromatography" was first described in detail by Small, Stevens and Bauman(25) in 1975. Its application to the analysis of atmospheric particulate samples was subsequently described by Rich(26) and by Mulik(27) at an EPA symposium in 1976. The technique is based upon classical ion exchange chromatography combined with a novel combination of resins and a universal conductivity detector. In conventional ion exchange chromatography with continuous effluent monitoring, the ionic species which are eluted from the chromatographic column are usually monitored by spectrophotometric methods. However, a large number of important anions and cations can not be determined in this manner due to their lack of appropriate chromophores. An ideal means of monitoring these ions might involve the conductance of the ions. Since ionic solutions must be used as eluants, however, the conductance of the eluant would ordinarily swamp the conductance of the sample ions. Small and coworkers overcome this difficulty by employing a combination of ion exchange resins to remove or neutralize the eluant ions, leaving the sample ions as conducting species in a non-conducting background. Since conductance is a universal property of ions in solution and is directly related to ion concentration, a simple and almost universal technique for determination of ion concentrations results. Details of the procedure may be found in Small, et al.(25)

Determination of Nitrate in Atmospheric Samples by Ion Chromatography

The original report by Small, et al.(25) demonstrated that nitrate could be separated and determined by ion chromatography. Subsequent reports by other investigators have characterized and documented the technique for determining nitrate in atmospheric particulate samples.

Mulik, et al.(27) described the successful use of ion chromatography for analysis of water soluble sulfate and nitrate in ambient particulate matter. They employed a D-ion-X Model 10 ion chromatograph with a 0.5μl sample loop. A minimum detectable quantity of 0.1μg/μl for sulfate and nitrate was reported with the 0.5μl loop. Relative standard deviations of 3 percent sulfate and 1 percent nitrate were obtained for replicate samples at concentrations of 5μg/ml.

Otterson(28) reported on the use of ion chromatography for determination of nitrate and other anions from upper atmospheric filter samples. The filters were collected as part of NASA's Global Air Sampling Program. The author reported success at determining NO_3^- as well as $SO_4^=$, F^-, and Cl^- at microgram levels and below. He described detailed procedures for cleaning and purifying the experimental equipment in order to obtain maximum sensitivity.

Lathouse(29) has described Battelle's experience with ion chromatography for NO_3^- and $SO_4^=$ determinations. Much of the NO_3^- data she discussed was collected during this program. These data, along with some more recent results, are presented below.

Experimental

A D-ion-X Model 10 ion chromatograph was employed in this investigation. The eluant was 0.003M $NaHCO_3$ and 0.0024M Na_2CO_3. A 0.1ml sample loop was used. Blank filter and water samples were run between each sample set. Filter samples were shredded and leached with deionized water on a steam bath for 2 hours. The samples were then cooled and filtered through 0.22 millipore filters. For some ambient samples, both hot water leaching and ultrasonic extraction techniques were employed. The results of these extractions are shown in Table 19. The agreement between the extraction techniques is excellent for sulfate and reasonably close for nitrate, with the exception of sample number 4. These data, when combined with the round-robin testing extraction and analysis results to be presented shortly, confirm the validity of the extraction procedure for nitrate and sulfate.

Accuracy and Precision

One evaluation of the accuracy of the ion chromatograph and extraction procedures is based on an Environmental Protection Agency interlaboratory study of nitrate and sulfate analyses. In this round-robin test, strips of glass fiber filters were sent to 60 laboratories. These laboratories extracted and analyzed the filters according to their normal operating procedures. Thus many extraction procedures and analytical methods were employed in the study. The results of this study are shown in Table 20.

TABLE 19. HOT LEACH VS ULTRASONIC FILTER EXTRACTION

Sample No.	Extraction Method	Nitrate, ng	Sulfate, ng
1	Hot Leach	1.57	2.32
	Ultrasonic	1.60	2.50
2	Hot Leach	1.96	3.05
	Ultrasonic	2.07	3.16
3	Hot Leach	0.87	2.35
	Ultrasonic	0.95	2.73
4	Hot Leach	2.64	12.8
	Ultrasonic	4.40	12.3
5	Hot Leach	1.28	16.1
	Ultrasonic	0.80	16.5

TABLE 20. RESULTS OF EPA PERFORMANCE AUDIT FOR NITRATE (concentrations in $\mu g/m^3$)

Sample No.	Battelle Ion Chromatograph	Sample Range	Target Range
1	11.780	10.374-11.466	9.282-12.558
2	11.100	10.374-11.466	9.282-12.558
3	5.250	4.912-5.428	4.395-5.945
4	5.420	4.912-5.428	4.395-5.945
5	2.250	1.843-2.037	1.649-2.231
6	7.650	7.011-7.749	6.273-8.487

Results which fall within the sample range indicate no detectable error. Results within this range are the best that can be expected under the conditions of the audit. The target range reflects the greatest variability that is expected during the audit, with the extraction and analytical process still operating properly. Results within this range indicate that the extraction and analytical procedures are valid. All but one of the ion chromatograph results fell within the target range and 4 of the 6 samples fell within the sample range. These results demonstrate the validity of both the extraction procedure and the ion chromatographic method.

A further evaluation of the accuracy of the ion chromatographic procedure made use of the widely employed brucine method as a reference. In these experiments, filter samples were extracted by hot leaching. The results of the brucine and ion chromatographic nitrate determinations on these extracts are presented in Table 21. The results show generally good agreement between the two techniques. The ion chromatographic results average about 3 percent lower than the brucine method. The relative deviation between the two methods averages about 9 percent.

Additional information on the accuracy and precision of the ion chromatographic procedure was obtained by analyzing prepared samples of two different nitrate salts and the extract from a high volume filter sample collected during the Phase III Los Angeles field study. Three different concentrations of each nitrate solution and the filter extract were run in quadruplicate by ion chromatography. The results of these analyses were shown earlier in Table 18 in the section on chemiluminescence. The ion chromatographic results were 3-7 percent below the prepared solution concentrations. The precision of the ion chromatographic data is excellent. The relative standard deviation is better than 1 percent in all cases and considerably better for most of the samples.

Comparisons of ion chromatography with our thermal decomposition/ chemiluminescence method were shown earlier in Table 18 and Figure 12.

Sensitivity

The sensitivity of the ion chromatograph with a new column and 0.1ml sample loop averages 0.09μg/chart division. This sensitivity projects a minimum detection limit of approximately 250 ng.

TABLE 21. COMPARATIVE NITRATE ANALYSES
(μg NO_3^-/Filter)

Sample	Brucine Method	Ion Chromatography
1	3.6	2.5
2	<5	5
3	6	5
4	11.0	10.0
5	15.0	20.0
6	18.8	20.0
7	24.0	25.0
8	37.0	38.5
9	45	47
10	46	45
11	58.2	65.0
12	117	140
13	122.5	145
14	190	211
15	240	245
16	342.5	750
17	680	750
18	1,060	1,060
19	1,650	1,650
20	15,600	15,250
21	22,000	20,870

With the larger 0.5ml sample loop, the detection limit is less than 100ng. As the column ages, the sensitivity changes considerably. As the column degrades with use, the retention times become shorter and the peaks taller. Thus the sensitivity improves at the cost of resolution. This variation in sensitivity with column age is shown in Figure 14. Although the sensitivity data in Figure 14 are based on peak height measurements, comparison of peak areas shows a similar trend. Because of this effect, standards must be run frequently and the column replaced as the resolution degrades. We currently run approximately 800 samples before column performance deteriorates to the point where a new column is required.

PHASE II SUMMARY

Our objective in this phase of the program has been to screen several prospective new methods for nitrate determination in atmospheric aerosol samples and to develop a method which is rapid, sensitive, selective, accurate and reproducible. A secondary goal has been to more fully characterize the new ion chromatographic method for nitrate determination.

Our initial screening of potential new methods for particulate nitrate determination included a gas-sensing electrode procedure and a thermal decomposition/chemiluminescence method. The investigation of the electrode procedure was terminated when it became apparent that the conversion of nitrate to nitrite (required for the electrode measurement) could not be carried out quickly enough on large numbers of samples to meet our criterion for rapid measurement.

The thermal decomposition/chemiluminescence method was developed, refined and extensively investigated. Two modes of operation were investigated. For greatest sensitivity, the nitrate sample can be decomposed by rapid heating to ~425°C and the decomposition products drawn into a nitrogen oxides chemiluminescence monitor. The chemiluminescence response is integrated, the peak area being directly related to sample concentration. For somewhat less sensitive but simpler and less expensive analyses, the decomposition products can be integrated by collection in a Tedlar bag, after which the NO_x concentration in the bag is determined by chemiluminescence. This concentration is also directly related to the amount of nitrate in the sample. No electronic integration apparatus is required in this mode. The detection limit of the former mode of operation is better than 10 ng NO_3^- in a 15 μl sample. The latter procedure can detect less than 50 ng NO_3^- in a 15 μl sample. The thermal decomposition/chemiluminescence method responds to NO_2^- as well as NO_3^-, although this is not a significant interference for atmospheric particulate samples. Interferences due to NH_4^+ and organic nitrogen compounds are eliminated by decomposing the sample in a nitrogen atmosphere. The apparatus can be assembled in 1-2 days and operated by a laboratory technician. Analysis time (excluding sample preparation) is approximately 7 minutes.

Our studies of ion chromatography indicate this technique is rapid, sensitive, selective, accurate and highly reproducible. With a 0.5 ml sample loop, ion chromatography can detect less than 100 ng of nitrate in a sample. The accuracy and reproducibility are excellent if the instrument is standardized frequently. Nitrate can be determined in the sample in less than 10 minutes. However, nitrate, sulfate, fluoride and chloride can all be determined in the same sample in less than 15 minutes. For atmospheric samples this is a major advantage over all other existing methods. Indeed, this is such a significant advantage that ion chromatography will very likely become the dominant method for atmospheric filter sample analysis. Our investigation indicates that the method is worthy of this growth.

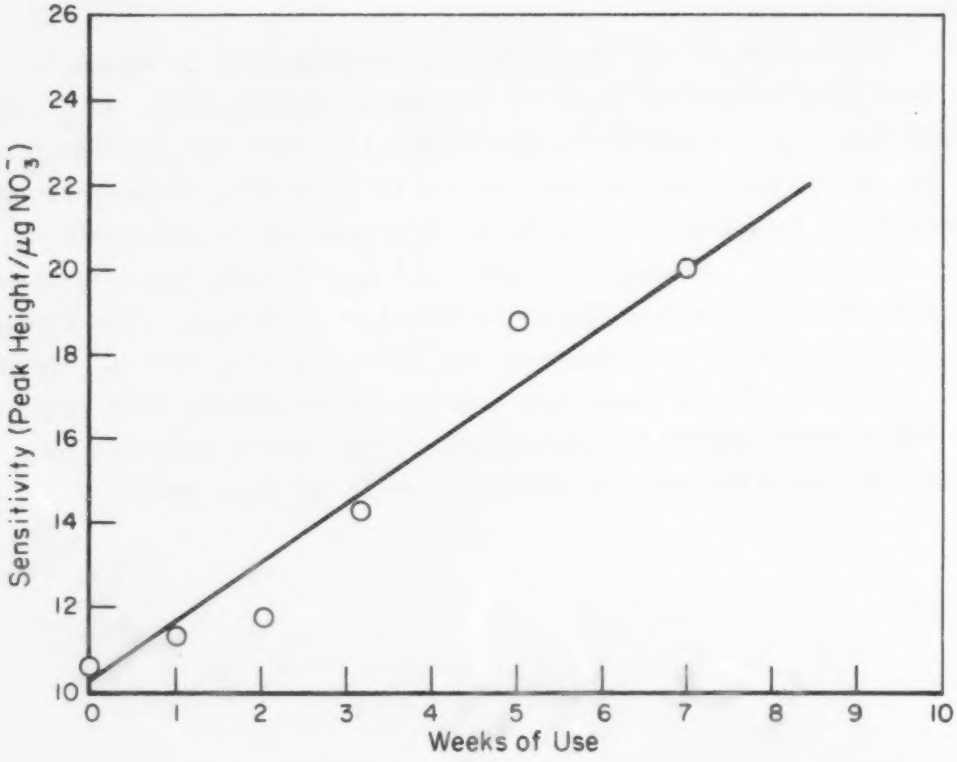


Figure 14. Nitrate Sensitivity vs Column age.

SECTION 4

PHASE III: FIELD EVALUATION OF SAMPLING MEDIA FOR NITRATE COLLECTION

In keeping with the program objective to investigate the effects of environmental variables on nitrate sampling, a laboratory study was conducted in Phase I of the program to determine the effects of filter composition, gaseous pollutants, sampling rate, sampling time, humidity, filtrate composition and storage time on particulate nitrate collection. While nitrate collection methods other than high volume sampling were considered, the Hi Vol method was given the greatest emphasis since it is already in such widespread use throughout the atmospheric sampling community.

A number of different filter materials were screened in the laboratory in an effort to uncover a material which would efficiently collect particulate nitrate with minimal interference due to trapping of gaseous nitrates or nitrate precursors. Subsequent to the laboratory screening studies it was deemed advisable to evaluate selected filter materials under actual field conditions and, at the same time, try to identify the variable or combination of variables which leads to artifact nitrate collection on certain filters. The ideal location for such a study is Los Angeles, where the precursors to artifact nitrate should be at a maximum(4). These conditions should provide the most severe test of filter materials. Since we were just organizing a field program in the Los Angeles area for another EPA project. "The Fate of Nitrogen Oxides in the Atmosphere and the Transport of Oxidant Beyond Urban Areas (Contract No. 68-02-2439)" a joint program was undertaken.

Experimental

The field program was conducted between October 15 and November 16, 1976. The overall study involved three ground stations and an instrumented aircraft. However, all the data pertinent to the present study were collected at our base station at Cable Airport in Upland, California. The base station consisted of the Battelle Mobile Air Quality Laboratory. The variables monitored at this location are shown in Table 22. The techniques used for these measurements are given in Table 23.

The base station was located approximately 37 miles east of downtown Los Angeles and less than 5 miles south of the base of the San Gabriel Mountains at an elevation of 446 meters above sea level. The location was selected because it lies along the normal wind trajectory from downtown Los Angeles. We expected to observe frequent episodes of well aged photochemical smog at this site. The meteorology varied considerably during the field program, from warm hazy weather to hot, dry, very clean desert wind conditions.

Aerosol samples were collected from 0900-1700 PST each day by three high volume samplers operating within the mobile lab. Samples were collected from 10 meters above ground using three 15cm diameter alumimum stacks. The aerosol was collected on 152mm diameter filters backed by a stainless steel fritted disk. One of these samplers was outfitted with a cyclone to remove particles with diameters greater than 2.0 μm. High purity quartz mat filters (Pallflex QAST) were always used with this sampler at a flow rate of 0.57 m^3/min.

The other two samplers were operated simultaneously in an identical manner at known flow rates of approximately 0.75 m^3/min. Pressure drop measurements were made at the beginning and end of each day's sampling to correct for day to day fluctuations in flow rate. Initial calibration of the high volume blowers was performed with a calibrated venturi. The filter material used in these samplers was varied from day to day among two types of quartz and two types of glass fiber filters. One or the other sampler (randomly varied) always operated with Pallflex QAST high purity quartz, which was used as a comparison standard. Thus one total aerosol sample and the small particle (<2.0 μm) sample are always collected on QAST and are directly comparable. Besides Pallflex QAST, the other three materials used in the high volume samplers include "EPA type" Gelman AA glass fiber filter, Gelman A glass fiber filter and a high purity quartz fiber filter developed by Arthur D. Little under contract to EPA. Each filter was preweighed in the laboratory at 40 percent relative humidity and then stored in an individual glassine

TABLE 22. MEASUREMENTS AT UPLAND STATION

Meteorological Measurements	Gas Measurements	Aerosol Measurements
Temperature	O_3	Mass Loading
Relative Humidity	NO	Nitrate
Solar Intensity	NO_x	Sulfate
Wind Speed	NH_3	Ammonium
Wind Direction	HNO_3	Total Carbon
	PAN	Total hydrogen
	Fluorocarbon-11	Total nitrogen
	SO_2	Nitrate $\leq$ 2.0 μm
	CO	Sulfate $\leq$ 2.0 μm
	CH_4	Ammonium $\leq$ 2.0 μm
	NMHC	Mass $\leq$ 2.0 μm
	C_2H_2	
	C_2H_4	

TABLE 23. ANALYTICAL METHODS

Determination	Instrument/Method	Calibration
O_3	REM Chemiluminescence Monitor	1% Neutral Buffered KI
NO	Bendix Chemiluminescence Monitor	NBS Cyl. "NO in N_2"
NO_2	Bendix Chemiluminescence Monitor	NBS Permeation Tube
HNO_3	Battelle Micro-Coulometric Instrument	Actual Samples of HCL and HNO_3
PAN	Electron Capture Gas Chromatograph	Actual Samples Referenced to I.R.
THC	Beckman Model 6400 Chromatograph	NBS Cyl. "Propane in Air"
CH_4	" "	Actual Sample Referenced to NBS Standard
C_2H_2	" "	" "
C_2H_4	" "	" "
CO	" "	NBS Cyl. "CO in Air"
NH_3	Dual Catalyst Chemiluminescence	Matheson Calibration Cylinder
SO_2	Flame Photometric	Permeation Tube
Fluorocarbon-11	Electron Capture Gas Chromatograph	Permeation Tube
NH_4^+ NO_3^- SO_4	High Volume Sampling/ D-ion-X Ion Chromatograph	Actual Samples
Wind Speed Wind Direction Temperature Relative Humidity	MRI Model 1071 Weather Station	
Solar Intensity	Eppley 180° Pyrheliometer	

envelope enclosed in a sealed polyethylene bag. After sampling, the filters were returned to their glassine envelopes and resealed in plastic bags. On return to the Columbus laboratories the filters were equilibrated at 40 percent RH and reweighed. The filters were then partitioned for analysis.

On many days during the study up to five different 47 mm filters were collected simultaneously from 0900-1700 PST. These filters were held by five 47 mm filter holders which were arranged circularly around and connected to one of the aluminum high volume stacks. All five filter holders were connected to a common vacuum manifold which was evacuated by a high capacity Gast pump. Pressure drop measurements were made several times each day on each filter. Flow vs pressure drop calibration curves were prepared for each filter type with a calibrated dry test meter and used with the pressure drop measurements to calculate flow. Total volume of air sampled varied between 3-11 m^3 depending on filter type. After collection, each filter was stored in a clean capped Petri dish.

All filters were extracted in deionized water over a steam bath. As described earlier in this report, this extraction procedure is quantitative for atmospheric particulate nitrates. The filter extracts were analyzed for NO_3^- and $SO_4^=$ by ion chromatography. A Dionex Model 10 ion chromatograph was operated in the manner described in Section III of this report.

RESULTS AND DISCUSSION

As mentioned earlier, three types of filter collections were made during the Los Angeles field study. These will be designated High Volume (152 mm diameter filters, 360 m^3), Low Volume (47 mm diameter filters, 3-11 m^3) and Small Particle (≤ 2.0 μm) samples. Both nitrate and sulfate were determined on these filters, and this section of the report will discuss both anions. However, primary emphasis will be placed on nitrates.

Results of High Volume Collections - Nitrate

The results of the duplicate Los Angeles filter collections for nitrate are shown in Table 24 where the nitrate concentrations from the QAST filters and the test filters are compared on a daily basis. On some days two

TABLE 24. COMPARISON OF NITRATE COLLECTED ON VARIOUS FILTER TYPES[a][b]

Date	Filter	NO_3^-, µg/m^3	Date	Filter	NO_3^-, µg/m^3	Date	Filter	NO_3^-, µg/m^3
Oct. 15	ADL	1.6	Oct. 26	ADL	1.3	Nov. 4	A	3.0
	QAST	1.6		QAST	2.1		QAST	1.1
Oct. 18	AA	14.4	Oct. 27	A	3.9	Nov. 5	A	6.1
	QAST	0.39		QAST	0.52		QAST	0.98
Oct. 19	AA	17.0	Oct. 28	AA	9.1	Nov. 9	A	8.4
	QAST	1.2		QAST	1.9		QAST	3.1
Oct. 20	AA	28.7	Oct. 29	ADL	1.8	Nov. 10	ADL	1.9
	QAST	2.3		QAST	2.9		QAST	2.3
Oct. 21	AA	18.8	Nov. 1	QAST	1.7	Nov. 11	QAST	2.0
	QAST	0.82		QAST	1.7		QAST	1.9
Oct. 22	AA	11.2	Nov. 2	A	9.1	Nov. 12	A	6.0
	QAST	0.49		QAST	1.6		QAST	1.3
Oct. 25	A	38.4	Nov. 3	ADL	0.68	Nov. 15	A	14.3
	QAST	0.78		QAST	1.1		QAST	3.0

(a) AA - "EPA Type" Gelman AA.
A - Gelman A

ADL - High Purity Quartz filter developed by Arthur D. Little under contract to EPA.

QAST - Pallflex QAST.

(b) Nitrate blanks for these filters were always <0.05 mg.

QAST filters were collected simultaneously on the two high volume samplers to test the equality of the samplers. The symmetry and equality of the high volume sampling systems are confirmed by inspection of the nitrate results from November 1 and 11 when identical quartz filters were employed in each sampler. Two different types of quartz fiber filters were compared on October 15, 26, and 29 and November 3 and 10. The two types of quartz filter generally collected nitrate concentrations of similar magnitude, with QAST tending to collect somewhat more nitrate than ADL.

The differences in nitrate concentration collected on glass versus quartz filters and the ratios of nitrate on glass and quartz are shown in Table 25. Since the filtration efficiencies for quartz fiber and glass fiber filters are the same, the differences in nitrate concentration in Column 1 represent artifact nitrate. For Gelman AA, artifact nitrate varied from 7.2 to 26.4 $\mu g/m^3$. Artifact collection on Gelman A varied from 1.9 to 15.3 $\mu g/m^3$. On the average Gelman A showed less artifact nitrate than Gelman AA. This may be attributed in part to the fact that less severe pollution conditions prevailed during most of the Gelman A collection days.

Plots of nitrate collected on the two types of glass filters versus the QAST filter are shown in Figure 15. Also shown is a plot of ADL versus QAST for the days on which these two quartz filters were collected simultaneously. The slope of the ADL vs QAST line is about 0.7 and the intercept approaches zero, suggesting some artifact collection on QAST. Our Phase I laboratory studies also suggested that QAST is slightly more susceptible to artifact collection than ADL. The intercept of the A vs QAST plot is also zero but the slope exceeds 5. Thus, on the average the A filter collects more than 5 times the nitrate collected by the QAST filter.

In constructing the AA vs QAST plot, one data point was ignored since it fell well outside the pattern formed by the other points. It is interesting to note that desert wind conditions prevailed on this day and that the relative humidity was less than half that measured on the other Gelman AA collection days. The effects of moisture and other environmental variables will be explored more fully later in this section. The slope of the AA vs QAST plot is nearly 8 and the intercept is 8.5. This curve implies considerably greater artifact collection for AA than A. Again, however, it

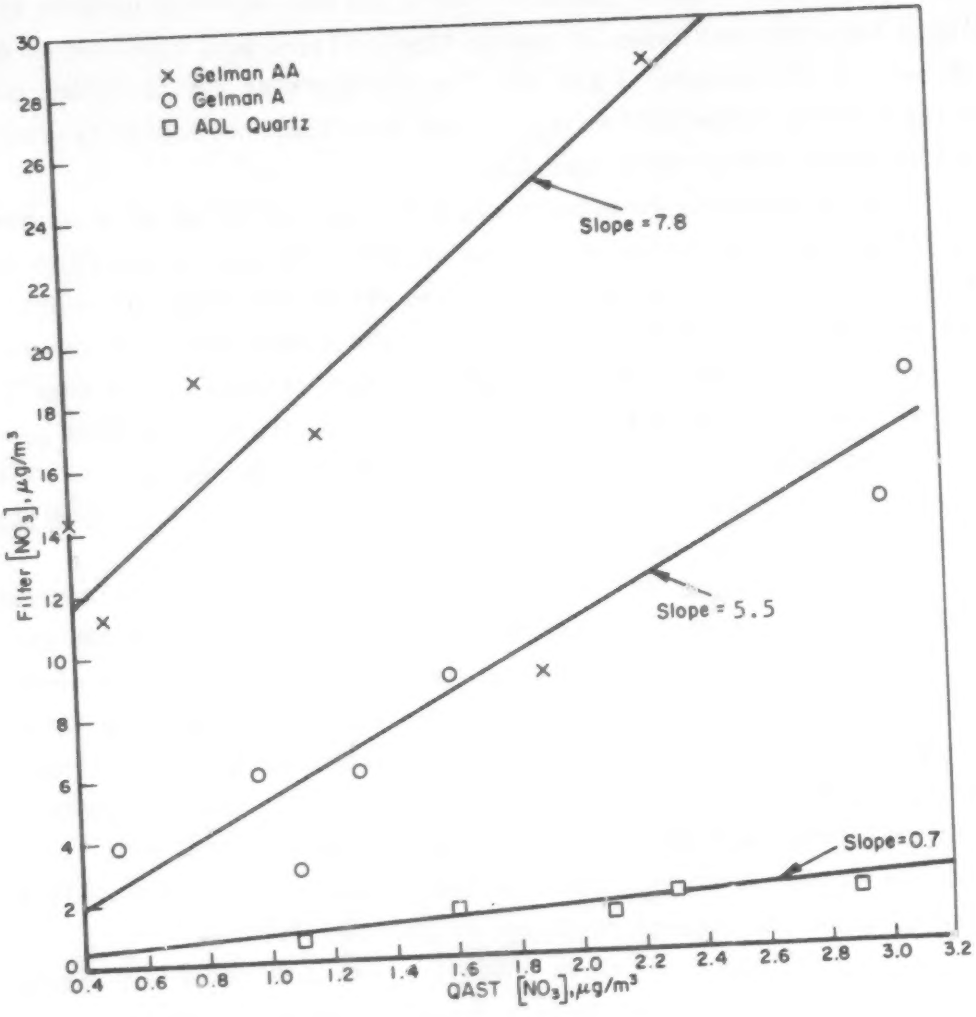


Figure 15. Simultaneous high volume nitrate collection results.

TABLE 25. COMPARISON OF NITRATE COLLECTED ON QUARTZ AND GLASS FILTERS*

	Gelman AA-QAST ($\mu g/m^3$)	Gelman AA/OAST
10-18-76	14.0	36.9
10-19-76	15.8	14.2
10-20-76	26.4	12.5
10-21-76	18.0	22.9
10-22-76	10.7	22.9
10-28-76	7.2	4.8
	Gelman A-QAST ($\mu g/m^3$)	Gelman A/QAST
10-27-76	3.4	7.5
11-02-76	7.5	5.7
11-04-76	1.9	2.7
11-05-76	5.1	6.2
11-09-76	15.3	5.9
11-12-76	4.7	4.6
11-15-76	11.3	4.8

*The results from 10/25/76 have been excluded here and in subsequent discussions due to a questionable analysis.

should be emphasized that the conditions thought to be favorable for artifact collection (e.g., high precursor concentrations and high relative humidity) occurred much more frequently during the Gelman AA collections. These differences in pollution conditions may partially explain the apparently large differences between the two glass filters.

The question arises whether the differences in nitrate collected on glass versus quartz filters could be attributed to differences in particle collection efficiencies. In general, both glass and quartz fiberous mat filters are claimed to have the same collection efficiencies are silimar is demonstrated by our sulfate results on the same filters. While the sulfate data will be discussed in more detail shortly, we observed similar concentrations on the various glass and quartz filters. Since more than 90 percent of the sulfate mass was found in the small particle size range (<2.0 μm), sulfate collection should represent a fairly severe test of filter efficiency. Because the glass and quartz filters exhibited similar collection efficiencies for sulfate, we can be assured that particle collection efficiency is not responsible for the large differences in nitrate collected on glass versus quartz.

Now that artifact nitrate collection has been documented under actual field conditions, it is enlightening to compare our Phase I laboratory results with the field data. Based on the saturation experiments and some other Phase I results, we concluded earlier that several of the 47 mm glass fiber filters saturate at 300-400 μg artifact nitrate. Due to differences in collection efficiency, saturation required about 8 mg NO_2 or 300-400 μg HNO_3. Experiments also suggested that the NO_2 collection efficiency increases with humidity, so that somewhat less than 8 mg NO_2 should result in filter saturation at ambient humidities. Extrapolating these values to the larger filters employed in our high volume field sampling, we find that ~140 mg NO_2 or ~6 mg HNO_3 is required to saturate the larger glass filters. Actually, less NO_2 would be required because of the higher NO_2 collection efficiency at ambient humidities. During our field study, NO_2 averaged 100 $\mu g/m^3$ and HNO_3 averaged about 7 $\mu g/m^3$. Therefore a typical glass fiber filter which sampled 360 m^3 of air was exposed to ~36 mg NO_2 and ~2.5 mg

HNO_3. The combination of these two gases should have resulted in about 70 percent filter saturation on the average. The filters may have been even closer to saturation due to higher humidities. Again extrapolating from the 47 mm filter laboratory results, 70 percent saturation of the larger filters should result in collection of ~4,400 μg artifact nitrate or

$$\frac{4{,}400\ \mu g\ NO_3^-}{360\ m^3} \simeq 12\ \mu g/m^3$$

of artifact nitrate. From Table 25, we actually observed an average of ~11 $\mu g/m^3$ of artifact nitrate, in rather close agreement with the prediction based on the laboratory study. While this crude exercise stretches the laboratory results beyond their intended purpose, it does serve to tie the laboratory and field studies together and demonstrates a fundamental correspondence in the results of the two.

Note that a high volume sampler collecting over a full 24 hours (rather than our 8 hour collections), would typically be completely saturated. As discussed in Section 2, a saturated 8" x 10" glass fiber filter which samples 2400 m^3 of air would suffer ~5 $\mu g/m^3$ artifact nitrate collection. While such filters may not normally saturate in many urban areas, still it is clear that even partial saturation results in significant errors in particulate nitrate measurement.

The nitrogen balance on the four high volume filter types is shown in Table 26. Within the rather wide scatter of the data the total amount of nitrogen on the filters (determined by an independent combustion/thermal conductivity procedure) is accounted for by the nitrogen present on the filter as nitrate and ammonium. The wide scatter in the data is caused by high total N backgrounds for the filters relative to the total N collected by the filters. Under these circumstances slight variations in the filter background or small errors in the total N analysis can have a major effect on the nitrogen balance calculation.

As seen in Table 26 the fraction of total nitrogen due to nitrate in 3-4 times higher on glass than quartz filters. This is an expected result of the collection of artifact nitrate by the glass filters.

TABLE 26. HIGH VOLUME FILTER NITROGEN BALANCES*

Filter Type	Number of Filters	Amount of Total N Accounted for by NO_3^- & NH_4^+, Percent	Amount of Total N Accounted for by NO_3^-, Percent
ADL	4	96 ± 40	17 ± 11
QAST	16	84 ± 22	18 ± 14
Gelman AA	6	111 ± 18	63 ± 29
Gelman A	8	87 ± 20	78 ± 24

*Filters for which the total N values were less than twice the filter background have been excluded.

Based on comparisons of the small particle samples with the total aerosol collections on QAST, about one half the nitrate mass was found in the particle size fraction less than 2.0 μm. The filter nitrogen balance for the small particle collections showed considerable scatter, but averaged 97 percent. If artifact nitrate due to a gaseous precursor were responsible for a large fraction of the nitrate observed on the QAST high volume filters, then the ratio of nitrate in the small particle size range to the total collected nitrate would be close to unity (since the gaseous precursor would pass through the cyclone). Instead, we observe a ratio of 0.5. This means that at least half of the nitrate collected on the QAST total filters must be true particulate nitrate of diameter ≥ 2.0 μm. Of course, considerably more than half of the nitrate collected on the QAST total aerosol filters must be true particulate nitrate since there must be small particle nitrate in the Los Angeles atmosphere. Indeed, most of the nitrate collected on the QAST filters could be true particulate, but the size distribution results can not confirm or deny this.

If it is assumed that the high concentrations of artifact nitrate found on the glass filters are due to a gaseous precursor, then such high concentrations would also be observed on glass filters backing up particle sizing devices. This would lead to the conclusion that the great fraction of ambient particulate nitrate mass is in the small particle size range, when in fact the actual particulate nitrate might be distributed in an entirely different manner. Since the health effects of nitrate particulates may well depend on size distribution, future studies must make certain that artifact collection not bias the size distribution results.

Results of High Volume Collections-Sulfate

Twenty one high volume sulfate sample pairs were collected at the Cable Airport site. Results of these collections are shown in Table 27. In these experiments, the primary reference filter was Pallflex QAST. The simultaneous collections on QAST November 1 and November 11 again confirm the equality of the sampling systems. Pairwise comparisons between QAST and ADL Microquartz, Gelman AA (EPA), and Gelman A are shown in Table 27. Also shown in the table are calculated values of the artifact sulfate, based on SO_2 and RH, as reported by Coutant(32). Calculated artifact

TABLE 27. HIGH VOLUME SULFATE RESULTS

Date	Filter[(a)]	$SO_4^=$ µg/m^3	$\Delta SO_4^=$ measured	ΔSO_4 calculated	Comment
10/15	ADL	27.2			
	QAST	36.9	-9.7	0.0	
10/18	AA	31.8			
	QAST	36.2	-4.4	1.1	No SO_2 data assume 50 ppb
10/19	QAST	32.1			
	AA	32.0	-0.1	0.95	No SO_2 data assume 50 ppb
10/20	AA	18.1			
	QAST	18.0	0.1	1.0	
10/21	AA	18.5			
	QAST	18.4	0.1	1.1	
10/22	AA	12.1			
	QAST	12.1	0.0	1.1	
10/25	QAST	19.8			
	A	21.5	1.7	1.0	
10/26	ADL	2.5			
	QAST	3.6	-1.1	0.0	
10/27	A	5.6			
	QAST	1.4	4.2	0.84	
10/28	AA	5.2			
	QAST	2.7	2.5	0.84	
10/29	ADL	3.9			
	QAST	5.2	-1.3	0.0	
11/1	QAST	3.4			
	QAST	3.5	0.1	0.0	
11/2	QAST	3.8			
	A	7.5	2.7	0.81	
11/3	QAST	3.2			
	ADL	2.0	-1.2	0.0	
11/4	A	4.9			
	QAST	1.4	3.5	0.78	
11/5	A	7.2			
	QAST	4.1	3.1	0.83	
11/9	A	11.8			
	QAST	9.2	2.6	0.81	
11/10	ADL	13.4			
	QAST	18.1	-4.7	0.0	
11/11	QAST	11.5			
	QAST	11.6	0.1	0.0	
11/12	A	10.4			
	QAST	5.2	5.2	1.5	
11/15	A	9.4			
	QAST	5.6	3.8	0.93	
	MEAN		0.85 ± 2.7	0.65 ± 0.49	

(a) QAST = Pallflex QAST Quartz
ADL = ADL Microquartz
AA = Gelman AA (EPA Type) Glass
A = Gelman A Glass

sulfate values are generally smaller in magnitude than those actually measured, but seem to correlate qualitatively except in the comparison of QAST and ADL filters. In this case, the ADL filter consistently yielded lower total sulfate levels than the QAST filter. Coutant(32) has reported that the collection of artifact sulfate by these two filter media was nearly equivalent. The current results may be due to batchwise variations in the nature of the QAST filter.

The sulfate results are shown in the form of average differences in Table 28. From this table, it is clear that the Gelman A filter yielded higher sulfate values than the QAST filter. The Gelman AA filter is approximately equivalent to the QAST, although there is somewhat more scatter in the data for this pair. Finally, the ADL filter response is consistently less than that of the QAST.

These differences in filter response for sulfate are further illustrated in Figure 16. This figure suggests that the responses of the Gelman AA and ADL filters are simple multiples of those obtained for the QAST filter. However, the data for the Gelman A filter do not extrapolate through the origin, suggesting that an additional source of error exists with the use of this filter. This behavior is similar to that observed with the AA filter for nitrate.

Low Volume Filter Sample Results - Nitrate

On Many days during the Los Angeles field study up to five different 47 mm filter samples were collected simultaneously from 0900-1700 PST at the mobile laboratory at Cable Airport. These samples were collected from one of the aluminum high volume sampler stacks, which sampled air approximately 10 meters above ground.

These filters were collected at low flow rates, the rate depending on the resistance to flow of each filter type. The low resistance filter (quartz and glass) were collected at flows between 0.012 and 0.023 m^3/min., with occasional exceptions, and the high resistance filters (Duralon, Mitex, Fluoropore) at flow rates around 0.008 m^3/min. At these flow rates, about 4 m^3 of air passed through the high resistance and 6-11 m^3 through the low resistance filters. With nitrate averaging only 1.5 $\mu g/m^3$ (as determined from the high volume collections on quartz), these low volume filters were generally collecting only low microgram quantities of nitrate. In many

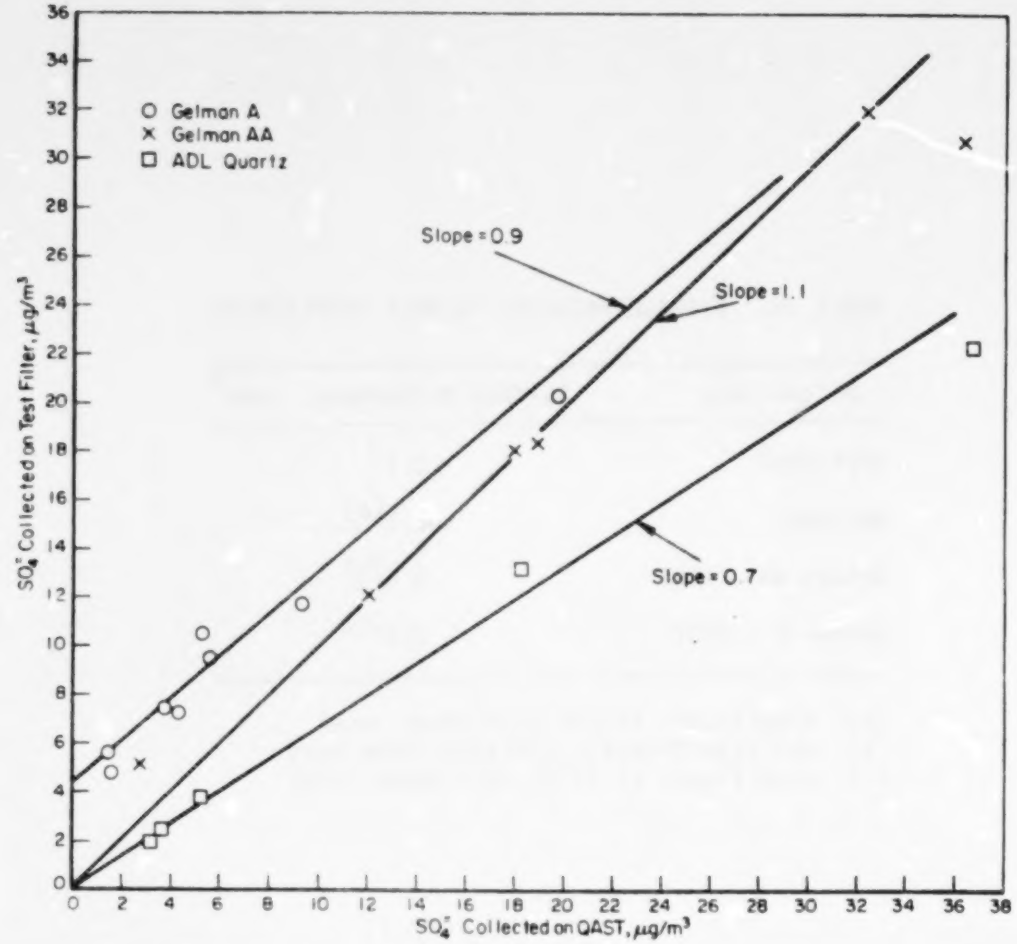


Figure 16. Comparison of filter sulfate responses.

TABLE 28. AVERAGE PAIRWISE SULFATE DIFFERENCES

Filter Pair	Sulfate Difference, μg/m^3
QAST-QAST	0.1
ADL-QAST	-2.1(a)
Gelman AA - QAST	-0.3(b)
Gelman A - QAST	3.4(c)

(a) significant at 90% confidence level
(b) not significantly different from zero
(c) significant at 99.5% confidence level

cases these low levels approached the limits of detection of the analytical methods being used. The concentrations of nitrate on many of the filters are not much greater than the filter nitrate blank, so any contamination or small filter-to-filter variations in nitrate blank can have a major effect on the calculated atmospheric particulate nitrate concentration. For these reasons the low volume filter data are not highly accurate and should be viewed with caution.

A bar graph showing the ratio of nitrate collected on several different filter materials relative to nitrate on ADL quartz is presented in Figure 17. The number of low volume filter pairs available for this comparison is shown for eacn filter type in parentheses. Mitex and fluoropore filters were included in these filter experiments but only two comparisons with Mitex and one with Fluoropore are available, and these occurred on days when the nitrate concentration was very low. The resulting large uncertainties have convinced us to forego quantitative comparisons with these two filters. Qualitatively, both filters seemed to collect greater amounts of nitrate than the quartz filters. This is surprising in light of our Phase I laboratory results, but may be due to the relatively large uncertainties in the data and the limited number of samples for comparison.

Figure 17 indicates that, for the environmental conditions, flow rates and face velocities employed during these experiments, Pallflex quartz collects slightly more nitrate than ADL quartz. The glass fiber filters all collect between 1-1/2 and 2-1/2 times as much nitrate as ADL quartz. The Duralon filter collected the most nitrate of all, as expected. We have demonstrated previously(33) that nylon filters quantitatively collect gaseous nitric acid. Nylon filters were used during the study for this purpose. Comparison of the nylon and ADL quartz filters suggests an average nitric acid concentration of about 0.002 ppm during the three days when data are available for comparison.

The days on which any given filter type was used for low volume sampling were randomly distributed during the field study. Therefore, due to daily variations in environmental conditions (precursor concentrations, RH, etc.) some filter types may have been exposed to more severe conditions than

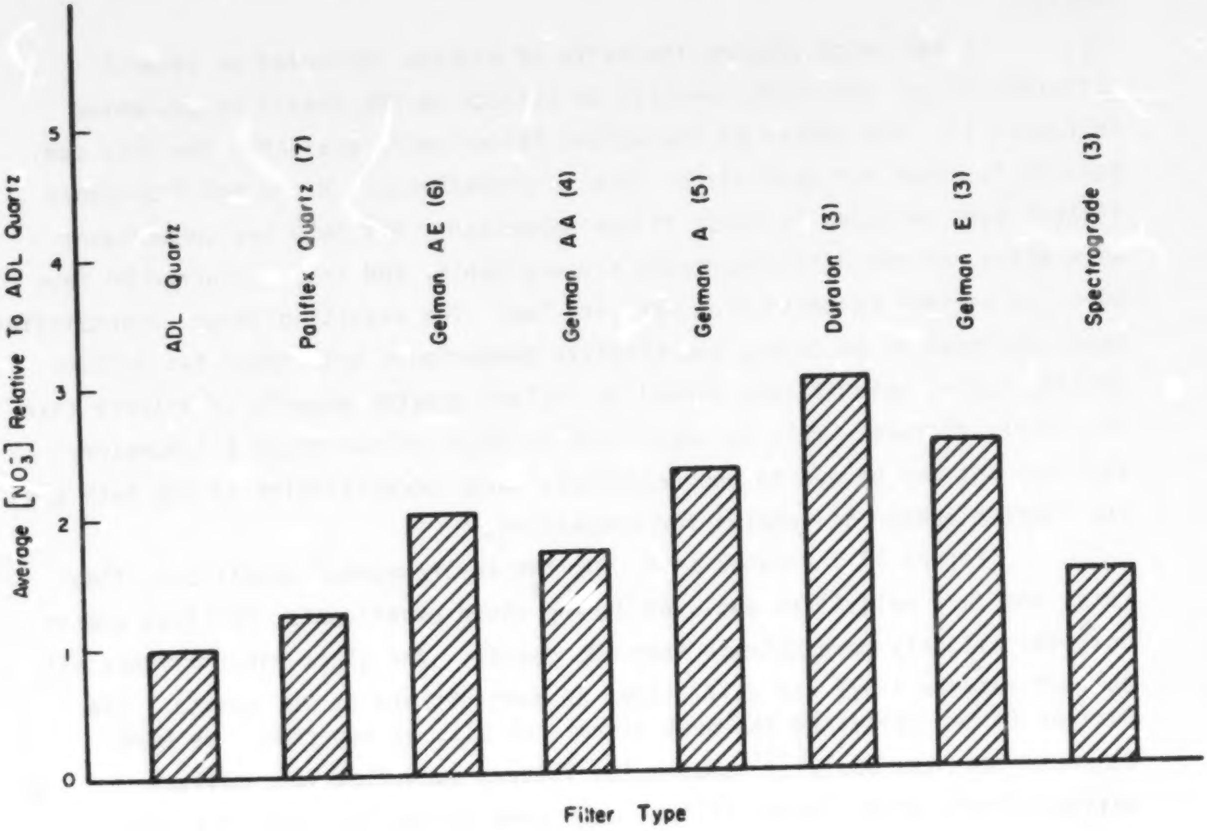


Figure 17. Relative nitrate collection for low volume filters.

others. In order to increase the number of filter pairs available for comparison, and thereby reduce potential distortions in the Figure 17 data due to daily variations in environmental conditions, the ratios were recalculated using either ADL or Pallflex quartz as the comparison standard. On days when data were available for both quartz filters, the average was used. Use of test filter/quartz ratios increased the number of days available for comparison, but the relative results were almost identical to those shown in Figure 17.

A quantitative comparison of the low volume and high volume nitrate results would be misleading and will not be undertaken due to the aforementioned inaccuracies in the low volume data. The low vol sampling was designed to screen a number of different filter materials for artifact collection under actual field conditions, and it served that purpose. However, such low levels of nitrate were collected during the 8-hour sampling period, that analytical imprecision and variations in filter blanks resulted in considerable scatter in the data. For this reason, we recommend that even the relative results of Figure 17 be viewed with caution.

Low Volume Sample Results-Sulfate

The low-volume sulfate results are derived from the same 47 mm filters just described, and the same caveats apply. The results of sulfate collections on various filter materials is shown in Figure 18 in bar-graph form. The ratio of the average sulfate on the test filters to the average sulfate on ADL quartz is depicted in the figure. The number of sampling days available for averaging is shown in parenthesis.

Pallflex quartz and Spectrograde glass both collect, on the average, the same concentrations of sulfate as ADL quartz. This can be compared to the Hi Vol. sulfate results where Pallflex quartz tended to collect somewhat more sulfate than ADL. The Gelman A, AA and AE filters and the Duralon Filter average 1.5-2 times the sulfate collected by ADL quartz. Gelman E collects over three times as much sulfate as Spectrograde or either of the quartz filters.

As discussed with the nitrate low volume sample results, the days for which comparative samples are available were randomly distributed during the study. Therefore some filters may have been exposed to more severe

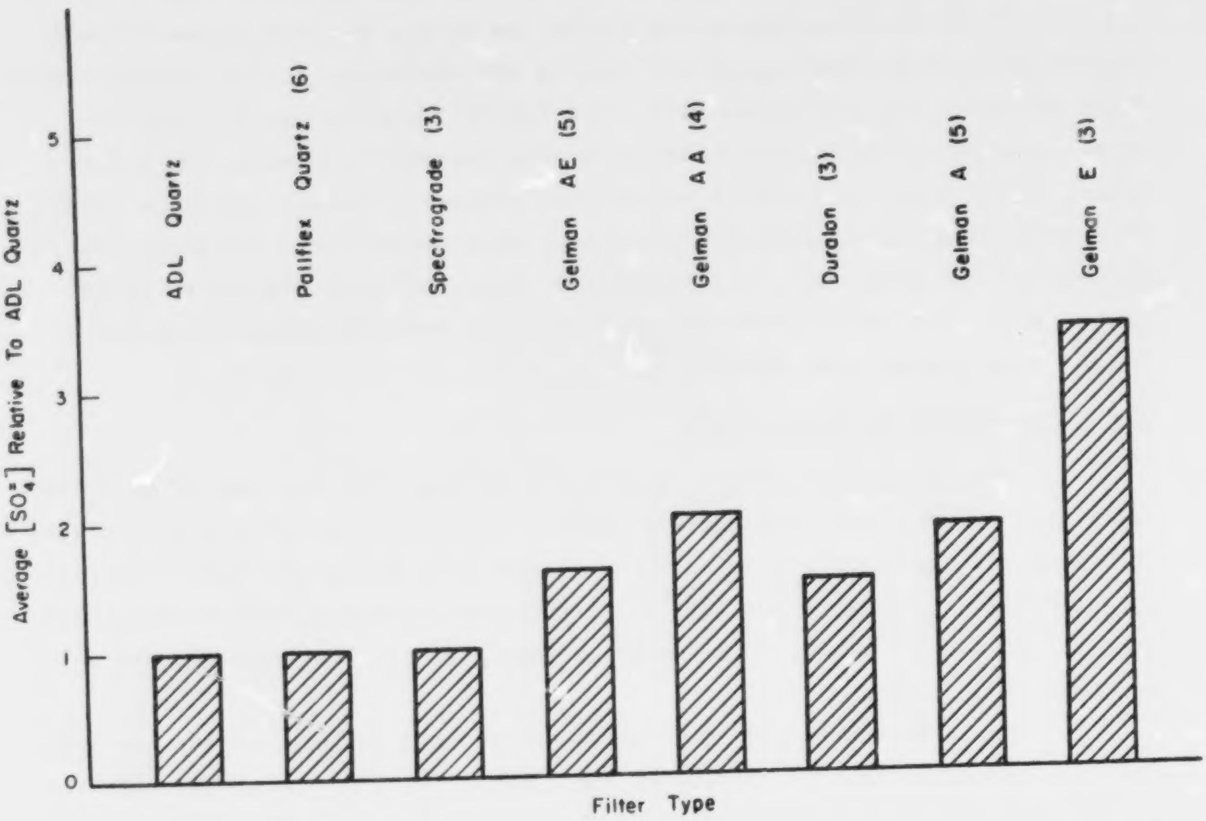


Figure 18. Relative sulfate collection for low volume filters.

conditions (higher SO_2 and RH) than others. For this reason, the relative sulfate collection ratios shown in the figure may be somewhat distorted. To minimize this distortion, we computed the sulfate ratios of the test filters versus either ADL or Pallflex quartz. Since Figure 18 shows the two quartz filters have equal collection efficiencies, the approach should be valid, and it increases the number of sample days available for averaging, thereby ameliorating the distortion caused by day to day variations in environmental conditions. In fact, this procedure yields results almost identical to those shown in Figure 18.

Identity of the Nitrate Precursor(s)

It is interesting to speculate on the precursors or environmental conditions which lead to artifact nitrate collection on glass filter media. Our Phase I laboratory studies suggested that a number of nitrogen containing gases, including NO, N_2O, NH_3 and PAN were unlikely precursors to artifact nitrate. The gases which did appear to be collected as nitrate by glass filters included nitrogen dioxide and nitric acid. The collection of these gases increased with humidity. Nitrogen dioxide had a much smaller effect on Gelman Spectrograde than the other glass fiber filters, probably due to the surface treatment of this filter. Nitric acid had a strong effect on Spectrograde, even though the filter is almost pH neutral. We suggested earlier that a different mechanism, involving acid attack of the surface coating, may be occurring with the Spectrograde filter. Since Spectrograde appears to differentiate between NO_2 and HNO_3, it may be a useful indicator of the artifact nitrate precursor. This possibility will be discussed shortly.

As an initial attempt to identify the environmental variables which foster artifact nitrate collection, the daily variations of a number of measured variables were plotted for the Los Angeles field study in Figure 19. Artifact nitrate (i.e., $[NO_3^-]_{GLASS} - [NO_3^-]_{QAST}$) is shown in the upper portion of the figure. Variations in artifact nitrate can be compared to the patterns of the other variables shown in the figure, including NO_2, relative humidity, average O_3, average PAN, NO_x plus PAN, and particulate nitrate (on QAST). Nitric acid is not shown in the figure since its concentration, as measured by microcoulometry, never exceeded the detection limit of about 6 ppb. The nylon filter technique, which was disucssed earlier, was also employed for nitric acid collection on six study days (10/22, 10/26, 11/2, 11/4, 11/9 and 11/15). The daily average (8 hour) concentration ranged from 1-5 ppb and averaged 2.6 ppb (6.7 $\mu g/m^3$). Therefore, the concentration of gaseous nitric acid was high enough to significantly affect the glass fiber filters. We have found in the past that gaseous nitric acid concentration is highly correlated with PAN(11). Thus, the behavior of PAN in Figure 19 should also qualitatively represent nitric acid.

It is clear from Figure 19 that several variables display patterns which are similar in many resepcts to the artifact nitrate pattern. Nitrogen dioxide seems to resemble the artifact nitrate behavior most closely. Ozone and PAN (or HNO_3) show similarities but also significant differences. The concentration of nitrate collected by QAST quartz, which we will assume represents actual particulate nitrate, also shows some similarities to the artifact nitrate pattern. It is unlikely that this signifies a cause/effect relationship; most likely, particulate nitrate is serving as a stand-in for other nitrate precursors. When the particulate nitrate concentration is high, nitrate precursor (and artifact precursor) concentrations are also likely to be high. As an example of this, the nitrate and NO_2 profiles are similar.

Interestingly, the relative humidity appears to be negatively correlated with artifact nitrate. This was not predicted by the laboratory results, which indicated a positive relationship. Since some variables, such as NO_2 and relative humidity, are apparently interacting, a more comprehensive statistical investigation of these effects was undertaken.

To investigate potential interactions among the variables, the data were scanned using the Automatic Interaction Detector (AID) statistical program. The details of this routine have been described by Sonquist and Morgan(34). Briefly, the technique identifies which independent variables are the best

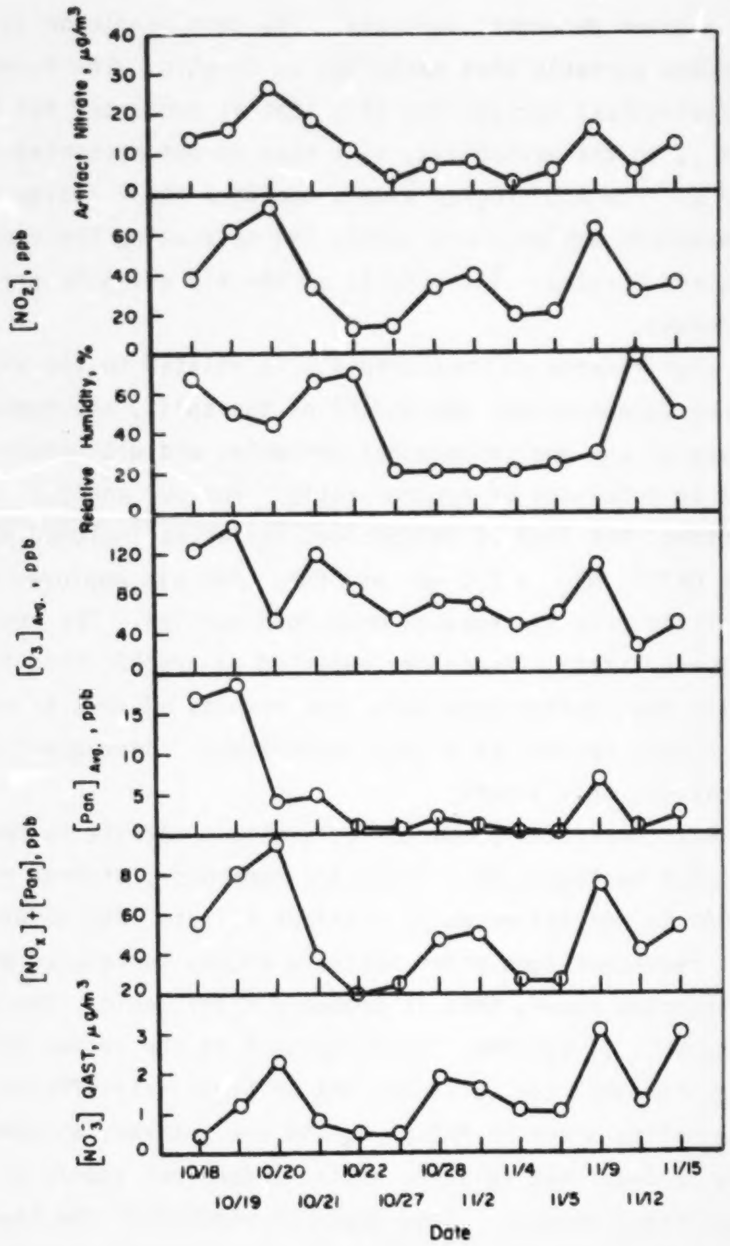


Figure 19. Daily variation of measured variables.

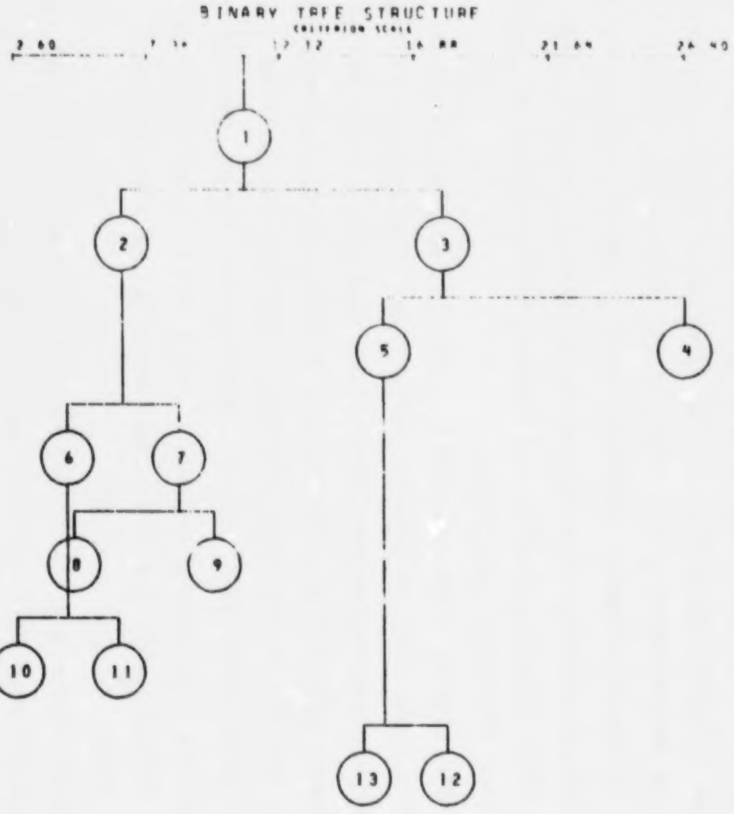
predictors of a given dependent variable. The best predictor is defined as the independent variable that maximizes an F-ratio. The F-ratio is the ratio of the statistical variability of y that is accounted for by the variability of χ, to the variability of y that is not accounted for by the variability of χ. The AID program simply computes the F-ratios associated with each independent variable and splits the data using the variable that yields the maximum F-ratio. The results of the AID analysis are reported in graphic-tree format.

The significance of the AID splits is related to the size of the data base, the extent (graphically, the width) of the split, the number of times splitting occurs on any one independent variable, and ultimately, the between sum of squares to total sum of squares ratio. For our analysis of artifact nitrate predictors, the list of independent variables included NO_2, humidity, O_3, NO_3^- (from QAST), $NO_3^- \leq 2.0$ μm, and PAN. PAN was employed primarily as a stand-in for nitric acid for reasons described earlier. The results of the AID analysis for artifact nitrate are reported in graphic-tree format in Figure 20. With the limited data base, the results of this or any other statistical analysis can not be highly significant. Consequently, we will discuss the analysis only briefly.

The most important predictor of artifact nitrate is PAN, as shown in the first split in Figure 20. Since the laboratory studies have demonstrated that PAN is not collected as artifact nitrate, PAN as an artifact nitrate predictor must represent some other variable highly correlated with PAN. For the reasons discussed above, this is probably nitric acid. The second split was a tie among NO_2, O_3 and PAN. Since Group 4 of the second split contains only one value, however, the split may not be highly significant. The remainder of the splits occur on PAN or O_3 and are not very enlightening. It is interesting to note that relative humidity does not appear as a significant predictor of artifact nitrate. This does not agree with the Phase I laboratory results, but the lack of a visible relative humidity effect may be due to the quite limited data base.

The results of the AID analysis generally confirm our earlier identification of nitric acid and NO_2 as the principal artifact nitrate precursors. It is not possible from our data to determine the relative contributions of NO_2 and HNO_3 to the amount of artifact nitrate collected by the glass filters.

AUTOMATIC INTERACTION DETECTOR
ARTIFACT NITRATE



SUMMARY TABLE

---TOTAL GROUP---
CRITERION - Artifact Nitrate
TOTAL GROUP N = 13
MEAN = 10.87
STD. DEV. = 6.67

PARENT 1 SPLITTING VARIABLE - PAN	
MEAN= 6.47 S.D.= 3.13 N= 8 PREDICTOR VALUES -- 0 1 2 3	MEAN= 17.90 S.D.= 4.44 N= 5 PREDICTOR VALUES -- 4 5 7 17 19
PARENT 3 SPLITTING VARIABLE - NO_2, O_3, PAN	
MEAN= 15.77 S.D.= 1.94 N= 4 PREDICTOR VALUES -- 5 7 17 19	MEAN= 26.40 S.D.= .00 N= 1 PREDICTOR VALUES -- 4 FINAL GROUP
PARENT 2 SPLITTING VARIABLE - PAN	
MEAN= 4.47 S.D.= 2.00 N= 4 PREDICTOR VALUES -- 0	MEAN= 8.47 S.D.= 2.48 N= 4 PREDICTOR VALUES -- 1 2 3
PARENT 7 SPLITTING VARIABLE - O3	
MEAN= 4.70 S.D.= .00 N= 1 PREDICTOR VALUES -- 0 FINAL GROUP	MEAN= 9.73 S.D.= 1.01 N= 3 PREDICTOR VALUES -- [illegible] FINAL GROUP
PARENT 6 SPLITTING VARIABLE - O3	
MEAN= 2.69 S.D.= 0.75 N= 2 PREDICTOR VALUES -- 10 19 FINAL GROUP	MEAN= 6.30 S.D.= 1.70 N= 2 PREDICTOR VALUES -- 17 22 FINAL GROUP
PARENT 5 SPLITTING VARIABLE - PAN	
MEAN= 15.03 S.D.= 0.76 N= 3 PREDICTOR VALUES -- 7 17 19 FINAL GROUP	MEAN= 18.00 S.D.= .00 N= 1 PREDICTOR VALUES -- 5 FINAL GROUP

Figure 20. AID results for artifact nitrate.

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However, we can use the low volume filter results of Figure 17 to confirm that both NO_2 and HNO_3 must be involved. We found in Phase I that Spectrograde filters were not significantly affected by NO_2 but were very seriously affected by gaseous nitric acid. Since Figure 17 shows that Spectrograde filters collected more nitrate than quartz during the field study, nitric acid must be responsible. Furthermore, since the other 4 types of glass filters collected even more nitrate than Spectrograde, NO_2 must also be contributing. While this is an admittedly crude test, it tends to confirm that both NO_2 and HNO_3 were contributing factors in the collection of artifact nitrate.

PHASE III SUMMARY

The objective of this phase of the program has been to evaluate, under field conditions, filter materials which the Phase I laboratory studies deemed potentially promising nitrate collection media. While both quartz and Teflon filters scored high in the laboratory investigations, our subsequent efforts emphasized quartz. The primary reason for this is that quartz filters, if found suitable, could be readily adapted for use in the extensive high volume sampling networks now in existence, whereas other considerations, such as pressure drop and electrostatic properties, make Teflon filters less desirable substitutes.

The field studies were conducted in the Los Angeles basin in order to provide a stern test of nitrate collection. The results of the field studies confirm the laboratory predictions that glass fiber filters collect considerably more nitrate than quartz filters due to collection of gaseous nitrogen species on the glass surface. Both high volume and low volume sampling demonstrated this effect. Artifact collection had the most serious impact on the high volume samples. Since we consider the Hi Vol data to be more reliable than the low volume results, we view artifact collection as a rather serious problem.

Both high volume and low volume results demonstrate that ADL quartz collects less nitrate than Pallflex QAST quartz. This agrees with the laboratory studies, which showed that QAST was slightly more susceptible to artifact collection than ADL.

Sulfate from both high volume and low volume sampling indicated some glass/quartz differences, but the differences were much smaller for sulfate than nitrate.

In the course of the Phase III study an attempt was made to identify the gaseous precursor(s) or environmental conditions which foster artifact nitrate collection. It seems likely that NO_2, HNO_3, and humidity all play a part in artifact formation, and that interactions among these variables are also important.

The field data suggest that previous studies of nitrate size distribution which employed glass fiber filters for collection may have yielded misleading size distributions due to artifact collection. Future studies should take great pains to eliminate this source of error, since the physiological effects of nitrate particulate are likely a function of size distribution.

Based on the Phase I laboratory studies (which demonstrated minimal artifact collection by ADL quartz) and the field results on artifact collection and size distribution, ADL quartz filters appear to collect particulate nitrate with only minimal interference due to artifact formation. The high and low volume field results also suggest minimal artifact sulfate collection on ADL quartz in agreement with the results of Coutant(32). For these reasons, ADL quartz (or equivalent) filters would be highly desirable replacements for glass filters in high volume sampling. Pallflex QAST quartz, a commercially available filter, is susceptible to some artifact collection, although it also is very much preferable to glass filters.

SECTION 5

PHASE IV: CONCLUSIONS REGARDING SAMPLING AND ANALYSIS OF ATMOSPHERIC PARTICULATE NITRATE

This report describes research on a number of different topics pertaining to the sampling and analysis of atmospheric particulate nitrate. The goals of the program have been to identify environmental conditions which affect nitrate sampling, to develop an improved sampling procedure and to conceive and develop an improved method for nitrate analysis. A detailed summary of each phase of the research may be found following each section of the report. A more general statement of the results and conclusions of the program follows.

This program investigated a number of potential sources of error in high volume nitrate sampling, including gas-filter interactions, gas-filtrate interactions, sampling rate, sampling time, storage time and gas-soot interactions. The collection of artifact nitrate by certain filter materials was found to be the most serious source of inaccuracy. Field results and extrapolations of laboratory data indicate serious interferences with particulate nitrate sampling, with both gaseous nitric acid and nitrogen dioxide contributing to the interference. Both the laboratory and field studies demonstrate that high purity quartz fiber filters represent a significant improvement over commonly used glass filters for high volume nitrate sampling. At least one type of quartz was shown to provide a relatively interference-free nitrate and sulfate collection medium.

A method for the analysis of such ambient filter samples for nitrate was developed during the program. The method is based on thermal decomposition of the nitrate, with chemilumnescent detection of the decomposition products. It is sensitive, accurate and very rapid. Ion chromatography was also investigated and found to be very well suited to the analysis of atmospheric filter samples. It is sensitive, accurate, reproducible and relatively rapid, and provides for simultaneous nitrate and sulfate determination. This latter feature makes ion chromatography the method of choice for the majority of ambient applications.

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APPENDIX

EXPERIMENTAL CONDITIONS

TABLE A-1. EXPERIMENTAL CONDITIONS AND SAMPLE VOLUMES
(VOLUMES IN m^3)

Experiment No.:	1	2	3	4	5	6	7	8	9
Experimental Conditions:	Clean Air	Clean Air	2.6 ppm NO_2	2.0 ppm NO_2	1.8 ppm NO_2 40% RH	1.4 ppm HNO_3	1.5 ppm HNO_3	8.0 ppm HNO_3	3.0 ppm HNO_3
Filter Materials									
Nylon (Duralon)	1.08	1.00	1.02(1.02)	0.99	0.87	0.76	0.99	1.29	1.32
Teflon (Mitex)	0.98	0.93(0.93)	0.92	0.91	0.79	0.69	0.89	1.22	1.22
Cellulose Acetate (Celotate)	0.95(0.95)	0.89	0.89	0.89	0.68	0.68	0.85	1.17	1.18
Glass (Gelman A)	1.12	1.05	1.02	1.02	0.79	0.79	1.00(1.01)	1.35	1.34
Glass (Gelman E)	1.12	1.03	1.03	1.03	0.79(0.79)	0.79(0.79)	1.00	1.35	1.37
Polycarbonate (Nuclepore)	1.07	1.00	1.00	0.97	0.75	0.75	0.96	1.31	1.28
Quartz (ADL)	1.12	1.04	1.05	1.01(1.03)	0.78	0.78	1.02	1.35	1.35

Experiment No.:	10	11	12	13	14	15	16	17	18
Experimental Conditions:	3.0 ppm HNO_3 30% RH	80 ppm NH_3	5.5 ppm NH_3	0.3 ppm PAN	15.6 ppm N_2O	18 ppm N_2O ~100% RH	1.7 ppm NH_3 40% RH	30 ppm NO_2 70% RH	11.5 ppm NH_3
Filter Materials									
Nylon (Duralon)	0.73	1.35	1.15	0.93	1.61	1.33	1.45	0.99(1.01)	—
Teflon (Mitex)	0.98	0.98	1.07(1.05)	0.82	1.52	1.25	1.34(1.36)	0.84	—
Cellulose Acetate (Celotate)	0.96	1.27	1.05	0.85(0.82)	1.45	1.17	1.29	0.91	1.29
Glass (Gelman A)	1.13	1.39	1.18	0.97	1.66	1.41	1.47	1.04	—
Glass (Gelman E)	1.13	1.39	1.20	0.97	1.67(1.64)	1.39	1.52	1.03	2.36
Polycarbonate (Nuclepore)	1.00	1.31	1.12	0.92	1.61	1.31(1.33)	1.40	0.89	—
Quartz (ADL)	1.13	1.41	1.20	0.96	1.64	1.41	1.50	1.03	2.37

TABLE A-2. EXPERIMENTAL CONDITIONS AND SAMPLE VOLUMES

Experiment No.	Experimental Conditions	Filter Material	Volume Sampled, m^3
19	0.024 ppm H_2SO_4	Glass (Gelman AE)	2.24
		Quartz (ADL)	2.29
		Cellulose Acetate	1.22
		Quartz (Pallflex)	2.30
		Quartz (ADL), clean	2.25
20	3.4 ppm HNO_3	Quartz (ADL)	3.68
		Glass (Gelman AE)	3.71
		Cellulose Acetate	2.24
21	19.5 ppm NO_2	Glass (Gelman AE)	2.14
		Cellulose Acetate	1.87
		Quartz (ADL)	2.10
		Quartz (Pallflex)	2.10
22	0.35 ppm HNO_3	Quartz (Pallflex)	4.15
		Quartz (ADL)	4.18
		Glass (Gelman AE)	4.09
23	21 ppm NO_2	Quartz (Pallflex)	0.95
		Quartz/Cellulose	0.98
		Glass (Gelman AA)	0.97
		Quartz (ADL)	0.98
		Glass (Spectrograde)	0.96
24	17.5 ppm HNO_3	Quartz (ADL)	1.25
		Glass (Gelman AA)	1.28
		Quartz/Cellulose	1.28
		Glass (Spectrograde)	1.28
		Quartz (ADL)	1.25
25	16.5 ppm NO_2 17% RH	Glass (Spectrograde)	1.26
		Quartz (ADL)	1.29
		Quartz (Pallflex)	1.29
		Quartz/Cellulose	1.30
		Glass (Gelman AA)	1.27